ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF ACRYLIC EMULSION POLYMER AND USING IN PAINT FORMULATION

M.Sc. THESIS

Elis KIRIMLI

Department of Polymer Science and Technology

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Thesis Advisor: Prof. Dr. Nilgün KIZILCAN

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

AKRİLİK EMULSİYON POLİMERLERİNİN SENTEZİ VE BOYA FORMÜLASYONUNDA KULLANIMI

YÜKSEK LİSANS TEZİ

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OCAK 2015

Elis Kırımlı, a **M.Sc.** student of ITU **Institute of Science and Technology/ Graduate School of Istanbul Technical University** student ID **515121008**, successfully defended the **thesis** entitled "**Synthesis of Acrylic Emulsion Polymerization and Using in Paint Formulation**" , which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my mom,

FOREWORD

The research work presented in this thesis has been carried out at Istanbul Technical University, Chemistry Department of Science & Letters Faculty, Resin-Pol Laboratory under the valuable and expert guidance of Prof. Nilgün Kızılcan.

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December 2014

Elis KIRIMLI
Chemical Engineer

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ABBREVIATIONS

VOC : Volatile Organic Compounds
MMA : Methyl methacrylate
2-EHA : 2-Ethylhexyl acrylate
SO_4^- : Sulfate
Fe^{2+} : Ferrous
Ag^+ : Silver
T_g : Glass transition temperature
UV : Ultraviolet
MFFT : Minimum Film Formation Temperature
NaOH : Sodium hydroxide
KOH : Potassium hydroxide
FT-IR : Fourier transform infrared spectroscopy
TFA : Thin Film Analyser
MAA : Metacrylic acid
AA : Acrylic acid
NMR : Nuclear magnetic resonance
PNVCz : Poly(Nvinyl) carbazole
Cz-MEKFR : Carbazole methyl ethylketone formaldehyde resin
PCz-MEKFR: Poly(Carbazole methyl ethylketone formaldehyde resin)
–COOH : carboxyl group
DIN : Deutsches Institut für Normung
EN : European Norm
ISO : International Organization for Standardization
H_2S : Hydrogen sulfide
EN : European Norm
ISO : International Organization for Standardization
ASTM : American Society for Testing and Materials
NaCI : Sodium chloride
APS : Amonyum persulfat
DPnB : Dipropylene glycol n-butyl ether
t-BHP : Tert-Butyl hydroperoxide
CIT/MIT : Chloroisothiazolinone / Methylisothiazolinone

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SYNTHESIS OF ACRYLIC EMULSION POLYMERIZATION AND USING OF IN PAINT FORMULATION

SUMMARY

Formed on the metal surface from corrosion due to the atmospheric conditions, causes the loss of the mechanical properties of the metal, reduce the lifespan and seriously affect the country's economy. For these reasons, metals have to be protected against atmospheric conditions. One of the precaution methods is isolated metals from water and air with a coating material. Solvent-based system is the leader of the metal coatings, but recently solvent-based product usage limitations and volatile organic compounds (VOC) regulations make popular water based coating for protection of metal. For that matter, solvent based products usage, which have negative effect on human health and environment because of toxic and flammable material inside can be reduced with water-based products. With the project, emulsion polymers performance which has ketonic resin as a co-binder will be tested on water based metal paint to evaluated corrosion and adhesion properties.

Ketonic resins can be added to the emulsion polymer to prolong coating life because it increases adhesion and corrosion performance. Ketonic resins are the family of thermoplastic resins and have low moleculer weight. They work as an adhesion promoter when combine with co-polymers. Cyclehexanone formaldehyde resin is used in this thesis because of high amount –OH functional group in its backbone. It gives better compability with water borne systems.

Choosing right polymer is one of the important criteria for corrosion protection. Emulsion polymerization system is can be used in the metal corrosion. 2-Ethylhexyl acrylate and methyl methacrylate can be choosen for polymerization due to their hard monomer properties.

Cyclehexanone formaldehyde resin is obtained solid state and it dissolved in proper solvent. This emulsion is added on pure acrylic polymer which, obtained from water based emulsion polymerization method, as 5% rate and tried to getting homogeneous blend under high-speed mixture. Acrylic polymer – ketonic resin blend is used for water-based metal coating formulation. Water based metal paint is applied on 4 different metal types such as aluminum, galvanized, stainless steel and cold rolled steel for checking adhesion and corrosion performances. The aim of the study is evaluating ketonic resin adhesion and corrosion performance on metal formulation with comparing ketonic resin-acrylic polymer combination and pure acrylic polymer emulsion without ketonic resin. For this study, 3 different paint is prepared one is has only pure acrylic polymer as a binder, second one is acrylic polymer – ketonic resin blend and last one is commercial product of ketonic resin is blended with acrylic polymer as a binder and cheching performance between 3 of them. According to adhesion and corrosion performances show that ketonic resin is enhance adhesion on some metal types: adhesion affects corrosion performance in long term. During the

synthesis part, when added ketonic resin on the system, some stability problem is observed. Although added some surfactant into the system for preventing agglomeration, is not clear off the problem. Preventing the system against to stability problem, resin will be connected with acrylic polymer as chemical bond during the polymerization stage and than they are tested on paint formulation is planned for next study. In this way, foreseeing that ketonic resin will be integrated the acrylic emulsion polymer and getting better adhesion and corrosion performances.

AKRİLİK EMULSİYON POLİMERLERİNİN SENTEZİ VE BOYA FORMULASYONUNDA KULLANIMI

ÖZET

Metal sahip olduğu yüksek performanslı özelliklerinden dolayı çevremizde görülen birçok yapıda kullanılmaktadır. Bu uygulamalar binalardan, köprü inşaatlarına, gemilerden, otomotiv sektörüne kadar geniş bir yelpazeye kapsamaktadır. Bu uygulamaların temel yapısını oluşturan metal, atmosferdeki oksijen, su ve nemden kolayca etkilenmekte ve bu etkilenme sonucu performansını kaybetmektedir. Atmosferik şartlardan dolayı metal yüzeyde oluşan pas, metalin mekanik özelliklerinin yitirilmesine neden olarak, kullanım ömrünü azaltmakta ve ülke ekonomisini ciddi bir şekilde etkilemektedir. Bu yüzden atmosferik şartlardan etkilenmemesi için her türlü metal için koruyucu önemler alınması gerekilmektedir. Korozyondan dolayı metal yüzeyde oluşan pas, metal içindeki demir iyonlarının hava ve su ile reaksiyon vermesi sonucu oluştuğu için, bu reaksiyonun önlenmesi ile metaller korozyona karşı korunabilir. Metal yüzey üzerinde oluşan bu reaksiyonu önlemek için çeşitli yöntemler kullanılmaktadır. Bu koruyucu yöntemlerden en yaygın kullanılanı ise, yüzeylerin kaplanarak su ve hava ile temasının kesilmesidir.

Kaplama, diğer bir ismi ile boya, su ve solvent bazlı olmak üzere iki çeşide ayrılabilmektedir. Metali atmosferik şartlardan korumak için uygulanan boya ya da kaplama malzemelerinde özellikle endüstriyel uygulamalarda solvent bazlı boya çeşidinin kullanımı hakimdi; fakat son dönemlerde, solvent bazlı ürün kullanımının kısıtlanması ve uçucu organik bileşen / volatile organic compound (VOC) kontrolü ile su bazlı ürünlerin hem teknik hem de yasal olarak ön plana çıkmalarına sebep olmaktadır. Böylece insan sağlığı ve çevre üzerinde olumsuz etkileri bulunan solvent bazlı ürünlerdeki zehirli ve parlayıcı maddelerin kullanımı, su bazlı ürünlere geçerek azaltılacaktır.

Tez aşamasında, korozyonu önleyici su bazlı bir boya formülasyonu üretilerek, korozyon ve yapışma performansı ISO standartlarına göre değerlendirilecektir. Boya formülasyonun ana bileşeni olan bağlayıcı, akrilik olacak ve emülsiyon polimerizasyon yöntemi ile sentezlenecektir. Polimerin yapışma ve korozyon direncinin iyileştirilmesi için ayrıca ketonik reçine sentezi yapılacak ve sisteme eklenmesi için çalışılacaktır. Yapılacak olan proje ile ketonik reçineler ile desteklenen su bazlı emülsiyon polimerlerinin metal kaplama boya formülasyonunda korozyon ve yapışma direnci test edilecektir.

Kaplama formulasyonlarına eklenebilecek son ilave ketonik reçineler, kaplamanın yapışma ve korozyon direncini arttırarak kullanım ömrünü arttırmaktadır. Ketonik reçineler düşük moleküler ağırlıklı ve termoplastik reçineler sınıfındadır. Genellikle polimerik maddelerle kullanıldığında, yapışmayı arttıcı ve parlaklık verici özelliklerini kopolimerlere taşırlar. Ketonik reçineler, keton ve aldehit monomerlerinin kimyasal reaksiyonu sonucu meydana gelmektedir. Bu reçineler üre, poliüretan, fenol gibi yardımcı hammaddeler ile desteklenerek performans özellikleri

iyileştirilebilmektedir. Akrilik polimer, su bazlı emülsiyon polimerizasyonu yöntemi ile sentezleneceğinden ketonik reçinenin su bazlı sistemlerler içinde kolayca çözünebilmesi ve homojen bir yapının oluşturulması gerekmektedir. Bu yüzden, siklo hekzan formaldehit reçinesi yapısındaki yüksek –OH grubundan dolayı seçilmiştir. Yapısındaki –OH grubundan dolayı su bazlı sistemlere daha kolay entegre olabileceği öngörülmüştür.

Su bazlı emulsiyon polimerlerinin sentezinde 2-EHA ve MMA gibi akrilik monomerler kullanılarak, metal kaplama malzemesine sertlik, yapışma ve kimyasal direnç özellikleri kazandırılmaktadır. Emulsiyon polimerizasyonu yöntemi kullanılarak çeşitli morfolojilerde polimer sentezi gerçekleştirilebilmektedir. Tez çalışmasında core-shell, çekirdek-kabuk, morfolojisi seçilmiştir. Core-shell morfoloji ile iki farklı özellik aynı polimer yapısında buluşturulabilmektedir. Çekirdek kısmında düşük *Tg* değerlerinde polimerler üretilebilmektedir. Bu sayede polimere elastikiyet ve düzgün film oluşturma özellikleri kazandırılmaktadır. Kabuk kısmında ise, daha sert monomerler kullanılarak polimere sertlik kazandırılmaktadır. Polimerin bu kısımda *Tg* değeri arttırılarak, polimere kimyasal direnç, UV dayanımı ve atmosferik şartlara karşı direnç özellikleri kazandırılabilmektedir. Tez aşamasında polimer morfolojisinin core-shell seçilmesinin nedeni ise, metal yüzeylerin sert oluşundan, korozyon direnci ve yapışma performansının iyi olması gerektiğinden yola çıkılarak seçilmiştir. Metal yüzey sert olduğundan dolayı üzerine uygulanacak kaplamanın düzgün film oluşturabilmesi için yeterince elastik olması gerekmektedir. Bu yüzden polimerizasyon aşamasında, ilk emülsiyon kısmında 2-EHA monomeri daha fazla eklenerek yumuşak bir çekirdek kısmı elde edilmiştir. Kaplama malzemesinin metali korozyona karşı koruması ve yüzeye iyi yapışması için daha sert olması gerekmektedir. Bu yüzden kabuk kısmı 2-EHA'ya göre daha sert olan MMA monomerinin daha fazla kullanılması ile elde edilmiştir. Bu çalışmada elde edilen saf polimer ile ketonik reçine yardımcı kimyasalı eklenen polimerin, metal boyasında korozyon ve yapışma direncine olan etkisi kıyaslanacaktır.

Polimer ve ketonik reçine sentezinin performans analizlerinin ölçülmesi için su bazlı metal boya formülasyonu dizayn edilmiştir. Bu formülasyon düşük Pigment Volume Consentration (PVC) değerine sahip, içerisinde polimer miktarı fazla olan bir formülasyondur. Formülasyonda korozyon engelleyici herhangi bir dolgu maddesi ya da katkı maddesi bulunmamaktadır. Böylelikle polimer ve ketonik reçine performansı daha kolay değerlendirilebilmektedir. Korozyon direncinin tayini için tuzlu suya batırma yöneti kullanılmıştır. Bu yöntemde paslanır metale uygulanan boyalar kürlendirildikten sonra, tuzlu suya batırılarak korozyon maruziyeti gözlemlenmektedir. Ayrıca boyalar, alüminyum, galvanize ve paslanmaz metale de uygulanmış ve ISO 2409 standardına göre ıslak ve kuru yapışma performansları değerlendirilmiştir.

Tezde 3 farklı boya üretilmiştir. İlk boya sadece akrilik polimerinin olduğu, içerisine ketonik reçine eklenmeyen boyadır. İkinci boya akrilik polimer ve sentezlenen ketonik reçine karışımı ile yapılmıştır. 3 numaralı boya ise akrilik polimer ve ticari olarak satışı bulunan ketonik reçine karışımı ile üretilmiştir. Amaç, ketonik reçinenin korozyon ve yapışmaya olan etkisini incelerken, diğer yandan sentezlenen ve ticari olarak satılan ketonik reçine arasındaki performans analizini de yapmaktır. Reçineler katı halde bulunduğu için polimere eklenmeden önce uygun bir çözücü ortamında homojen hale getirilmesi gerekmektedir. Katı halde bulunan siklohekzon fomaldehit reçinesi aseton gibi uygun bir çözücü ortamında öncelikle çözülmüştür. Bu reçine çözeltisi su bazlı emülsiyon polimerizasyonu ile sentezlenen akrilik bağlayıcı diğer

ismi ile polimere 5% oranında eklenerek homojen bir karışım elde edilmeye çalışılmıştır. Akrilik polimer – ketonik reçine karışımı, metal kaplama boyasına eklenerek metale doğrudan uygulanabilen bir boya elde edilmiştir. Elde edilen boya yapışma performansının değerlendirilmek üzere alüminyum, galvenize, paslanır ve paslanmaz metal olmak üzere 4 farklı metal üzerine aynı kalınlıkta uygulanarak, aynı şartlarda kürlenmeye bırakılmıştır. Korozyon performansının ölçülmesi için de sadece paslanır metallere uygulama yapılmıştır. Tüm boyalar oda şartlarında kürlendirildikten sonra yapışma ve korozyon kontrolleri gerçekleştirilmiştir. Çalışmada akrilik bağlayıcı kendi halinde, sentezlenen ketonik reçine ile karıştırılarak ve piyasadan alınan UK100 isimli ketonik reçine ile aynı oranda karıştırılarak 3 farklı boya elde edilmiştir. Bu 3 boyanın kendi aralarında performansı incelendiğinde, ketonik reçineli karışımların alüminyum ve paslanır yüzeylerde özellikle ıslak yapışmayı iyileştirdiği tespit edilmiştir. Sentezlenen ve ticari olarak satışı olan ketonik reçineler kendi aralarında kıyaslandığında, sentezlenen ketonik reçinenin daha iyi performansa sahip olduğu bazı metal tiplerinde görülmektedir. Korozyon direnci incelendiğinde de, yine ketonik reçinelerin korozyon direncini arttırdığı saptanmıştır.

Çalışma sırasında ketonik reçinenin akrilik emülsiyon karıştırıldığı sırada bazı stabilite problemlerine rastlanmıştır. Su bazlı emülsiyon polimerleri, ketonik reçineleri homojen ıslatamamıştır. Polimer-ketonik reçine karışımı içerisinde stabiliteyi bozan aglomerasyona uğramış ketonik reçine parçacıkları görülmüştür. Bunu önlemek için çeşitli yüzey aktif ajanların yanında non-ionic, yüksüz, sürfaktanlar da sisteme eklenmesine rağmen stabilite için yeterli bulunmamıştır. Bunun için ileriki aşamalarda reçinenin, akrilik polimerin hazırlanması sırasında akrilik polimere kimyasal olarak bağlanması ile elde edilecek akrilik polimer-reçine kopolimerleri hazırlanması ve boya forrmülasyonunda tekrar test edilmesi planlanmaktadır. Polimer emülsiyonu sırasında sisteme eklenecek olan ketonik reçineler, polimerler ile kimyasal bağ yaparak sisteme daha iyi entegre olabileceği öngörülmektedir. Böylece herhangi bir stabilite sorununun ve aglomerasyon probleminin engelleneceği varsayılmaktadır. Sistem ile daha iyi entegre olan ketonik reçinenin yapışmayı ve korozyon direncini daha da arttırması öngörülmektedir.

1. INTRODUCTION

Metals have high strength and outstanding mechanical properties so they are used wide range of industrial application areas. However, when they are exposed to a corrosive environment, they will corrode so their service life will reduce and lose their protective properties. This performance reduction causes a huge economic impact for all countries [1]. Protective of metal surface with some precaution methods are needed. Coating of metallic surface is on the most popular method. Generally, solvent borne system is selected for industry coating application for protecting the metal to corrosion. However, some environmental regulation factors and cost factors introduce water base system in the industrial application [1,2].

Despite steady progress of water borne system, they still need for improvements. Choosing right polymer is one of the important criteria for corrosion protection. Emulsion polymerization system is can be used in the metal corrosion [2]. Styrene, 2-EHA and MMA can be choosen for polymerization due to their hard monomer properties, having good elasticity, chemical and weathering resistance [3]. Co-polymer system can be selected for getting more and different specialty polymer. Core-shell morphology is selected to obtained not only hard and chemical resistance but also good elasticity, gloss and weathering stability [4]. Core-shell morphology is achieved by two different emulsion steps. First of all, core of the polymer is created by using softer monomer such as 2-EHA. 2-EHA has lower Tg value, so it makes flexible films at ambient temperature. It brings flexibility to coating material by polymer. So coating material can adhere easier to metal substrate than hard monomers. MMA is harder monomer than 2-EHA. It can be used for creating shell structure [4,5]. Hardness is important criteria for metal coating. It prevents the metals from environment conditions. Hardness effects directly to chemical resistance, adhesion and corrosion protection of metals. If a polymer is formed only soft monomer, it will not protect the surface from corrosion or its adhesion will not be good enough. Vice versa, if a polymer composes of only hard monomers, it will be

too brittle for covering substrate and getting a proper film formation and again metal will not protected against to corrosion [6].

Some adhesion promoter additives are added on polymer to improve adhesion on metal and they directly affect of metal life. Coating material must be adhere intensely on surface, otherwise metal will vulnerable to rust and lose to service life [7]. In coatings, ketonic resins are used in every case only as an accompaniment it other binders, for example in alkyd/acrylic coating materials, cement paints. Epoxy resin systems and marine paints. A further principal area of application is represented by adhesives and sealing compound. Ketonic resins improve adhesion properties by their hard specialty. Cyclohexanone formaldehyde resins are selected for coating industries to metal protection. In the water besed system, it is preferred because of their hydroxyl amount. It has much more hydroxyl amount than ketone-ketone or keton-aldehyde resins. High amount hydroxyl groups provide solubility on polar compound and compability with water based acrylic [8].

Synthesized polymer and ketonic resin will be formulated on metal paint. That way, polymer and ketonic resin performance will be proved with real applications. They will be used in high gloss paint formulation which have high amount binder amount for seeing the binder effect clearly. Synthesized ketonic resin and its commercial one will be examined with comparing pure acrylic resins and also ketonic resins will be compared with each other according to corrosion and adhesion performances.

2. THEORETICAL PART

2.1 Emulsion Polymerization

In emulsion polymerization, monomer mixtures are dispersed in water with the aid of suitable emulsifiers. The polymerization reaction, which takes place at elevated temperatures, is initiated by water-soluble initiators and occurs in micelles. The outcome is stable aqueous dispersions that are used for wall paints, house paints, adhesives, printing inks and textile treatments [9].

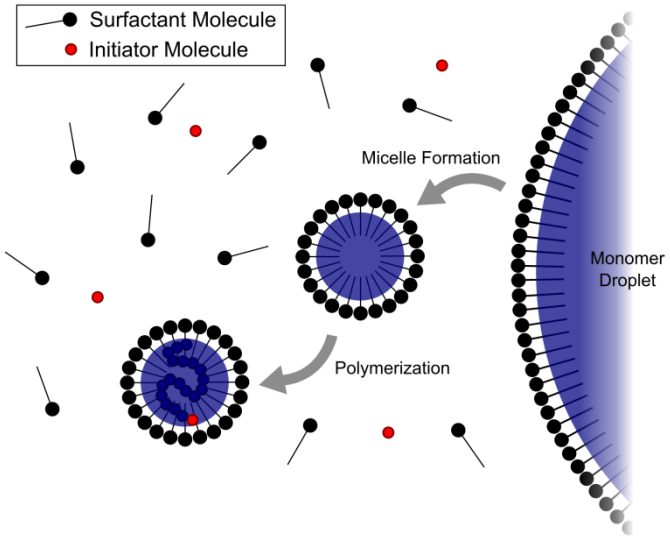


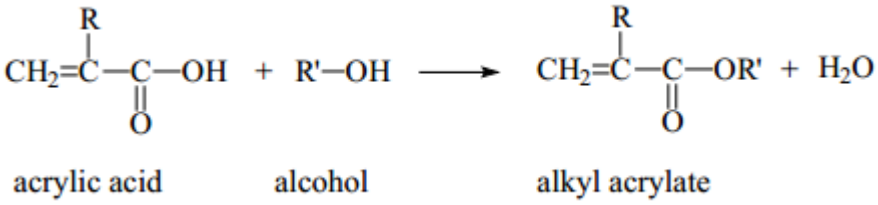
Figure 2.1 : Mechanism of emulsion polymerization.

Emulsion polymerization is a type of free-radical polymerization. Emulsion polymerization is carried out in water using monomers, surfactants (emulsified) and a water soluble initiator. As shown on the Figure 2.1. the monomers are emulsified in water with surfactant molecules oriented at the surface of the emulsion droplets, stabilizing the emulsion. There is also surfactants dissolve in the water and excess surfactant present in micelles. This polymerization is a chain reaction initiated by the decomposition of an initiator molecule. This initiator radicals attack the double bond of monomer and forming chain radicals. These radicals react with a further monomer molecule to produce extended chain radicals. The chain reaction continues to

propagate until the growth of the chains is terminated by recombination or disproportion [9,10].

The polymers which are produced by emulsion polymerization method, are manufactured from monomers. These monomers can be styrene, vinly and acrylics. Acrylics are esters of acrylic acids, that they are the products formed by the reaction of an acrylic acid and alcohol. They are widely used in the surface coatings industry. These are then polymerized using a radical initiator in a water emulsion [10,11].

Monomers, are prepared by a reversible reaction between an acrylic acid and an alcohol as shown below:



The major monomers used are ethyl acrylate, methyl methacrylate and butyl acrylate, as well as non-acrylic monomers such as vinyl acetate and styrene which behave similarly. Homopolymers latexes of these monomers have wide range of application areas such as paint, coating, textile, leather, construction etc. These polymers are stable, have good pigment binding capacity, durability, chemical resistance, impact resistance. Wide range of copolymers can be produced, and by varying the ratio of their monomers a series of polymers with a wide range of glass transition temperatures can be produced with emulsion polymerization method [10,11,12].

Surfactant can be called emulsified, is a substance composed of mutually repellent polar and non-polar ends. The aim of the surfactants are reducing the surface tension of water and facilitate the wetting of surfaces and the emulsification of organic substances in water. The surfactant surrounds each monomer droplet with a layer of surfactant with the polar tails oriented towards the surrounding water thus forming a micelle [12].

Water, is used as the medium to disperse and wet the micelles. During the emulsion polymerization process the water acts as a solvent for the surfactants and initiators, as well as a heat transfer medium [12,13]. Water based paints and solvent based paints are differentiated with regard to medium type, water or solvent.

The initiators (catalysts), usually used are water soluble peroxidic salts such as ammonium or sodium peroxydisulfate. The reaction can be initiated either by thermal or redox initiation. In thermal initiation the peroxydisulfate dissociates to give two SO_4^- radicals.

$$\underset{\text{peroxydisulfate}}{^-O_3S—O—O—SO_3^-} \rightarrow \underset{\text{sulfate radical}}{2SO_4^{-\bullet}}$$

In redox initiation a reducing agent (usually Fe^{2+} or Ag^+) is used to provide one electron, causing the peroxydisulfate to dissociate into a sulfate radical and a sulfate ion.

$$Fe^{2+} + \underset{\text{peroxydisulfate}}{^-O_3S—O—O—SO_3^-} \rightarrow Fe^{3+} + \underset{\text{sulfate radical}}{SO_4^{-\bullet}} + SO_4^{2-}$$

Straight acrylics are polymer dispersions composed exclusively of acrylate and/or methacrylate monomers. Styrene acrylic copolymers contain styrene as well. For both types of copolymer there are a host of monomers which differ greatly as regards glass transition temperature and the polarity of the homopolymers preapared from them [14]. Table 2.1 shows some monomer's water solubility and *Tg* values. Monomer composition is determined specify according to application conditions.

The special features of the polyacrylates and polymethacrylates that justify their relatively high price are the generally very good weatherability and UV stability, high transparency, good water resistance and yellowing resistance, great ease of variation in toughness, hardness and flexibility [15].

Special polymerization technique can be used in emulsion polymerization that comes from morphology of polymerization. Different kind of morphology is used in emulsion polymerization technology such as core-shell, raspberry, half-moon shaped particles. Core-shell technology is one of the most widely used methods in polymerization. By combining a soft, film forming occurs at low temperature, and a hard monomer, which film formation occurs at high temperature in one and the same particle, and by tailoring the particle morphology, it is even possible to achieve better polymer speciality. Such this core-shell system have a low MFFT and high eleasticity, along with good freedom from tackiness, excellent blocking resistance and good coating hardness. Especially for the special coating application systems

such as wood coating, metal coating, joinery, core-shell morphology is preferred [16,17].

Table 2.1 : Water solubilities and glass transition temperatures of the principal monomers for acrylic dispersions.

Monomer building blocks	Water solubility at 25°C in g/100 cm^3	Glass transition temperature (Tg) of the homopolymer °C
Acrylates		
Methyl acrylate (MA)	5.2	22
Ethyl acrylate (EA)	1.6	-8
n-Butyl acrylate (nBA)	0.15	-43
Methacrylates		
Methyl metacrylate (MMA)	1.5	105
n-Butyl metacrylate (nBMA)	0.08	32
Styrene	0.02	107
Acrylonitrile	8.3	105
Vinyl acetate	2.4	42

The special features of the polyacrylates and polymethacrylates that justify their relatively high price are the generally very good weatherability and UV stability, high transparency, good water resistance and yellowing resistance, great ease of variation in toughness, hardness and flexibility [15].

Special polymerization technique can be used in emulsion polymerization that comes from morphology of polymerization. Different kind of morphology is used in emulsion polymerization technology such as core-shell, raspberry, half-moon shaped

particles. Core-shell technology is one of the most widely used methods in polymerization. By combining a soft, film forming occurs at low temperature, and a hard monomer, which film formation occurs at high temperature in one and the same particle, and by tailoring the particle morphology, it is even possible to achieve better polymer speciality. Such this core-shell system have a low MFFT and high eleasticity, along with good freedom from tackiness, excellent blocking resistance and good coating hardness. Especially for the special coating application systems such as wood coating, metal coating, joinery, core-shell morphology is preferred [16,17].

2.1.1 Acrylic emulsion polymer

Acrylic resins are composed mainly esters of acrylic acids or methacrylic acid. They are generally used in paint and coating industries. Also they can be used in textile, adhesive, printing inks, paper coating and construction industries. Acrylic esters and methacrylic esters have quite different properties. Amount of these esters in polymer specify material properties, hardness, flexibility, chemical resistance, leveling during film formation [18].

Esters of acrylic acid or methacrylic acid are distinguished by the reactivity of their double bonds. After initiation these double bonds connect each other and polymerization occurs. Esters of acrylic acid and metacrylic acid which act as building blocks for polymers are called monomers. Further building blocks capable of forming polymers conjuction with acrylic and metacrylic esters are called comonomers [4,19].

Acrylic resins can be classified into two groups. First group called polyacrylates. These groups are prepared by polymerizing arcylic or methacrylic esters via their double bonds. Polyacrylates are also divided two groups according their polymerization process, solution polymerization and emulsion polymerization. With solution polymerization, polymerization process occurs in organic solution and this polymer can be used directly in coating formulation. In addition, such polymers can be transformed into secondary aqueous dispersion a powder coating resins. Another process is emulsion polymerization, monomer mixtures are dispersed in water with the aid of suitable emulsifiers. Emulsion polymerization will be detailed into the next sections [4,20].

The second group of acrylic resins for coatings comprises acrylic or methacrylic ester resins that still contain double bonds. These binders are called reactive acrylic resins. Addition or condensation reactions are employed to incorporate the acrylic or methacrylic ester into polymer or oligomer molecules. The resultant binders are capable of forming films by polymerization after application, and are mainly by energy-rich radiation which yields three-dimensional crosslinked macromolecules [21].

Water-borne acrylic dispersions are commonly prepared via emulsion polymerization. Emulsion polymerization has more advantages in comparison to solution polymerization. First of all, much higher molecular weight polymers can be synthesis. High solid content (50% or higher) polymers can be produced with emulsion polymerization. Another advantage is that the resin has low viscosity, thus allowing fast air drying by evaporation of water [5,22]. When developing dispersions for any application, one has to consider that emulsion polymers are "products-by-process" whose main properties are determined during the polymerization process. Therefore, a deep understanding of how to use the polymer microstructure (molecular weight distribution, polymer composition, branching and crosslinking density, particle morphology and particle size distribution) in order to affect the anticorrosive properties, is necessary. By designing the polymer architecture of the latex particles in a way that leads to better film forming, pigment distribution in the paint formulation and high barrier properties thus closing the performance gap versus their solvent-borne counterparts [23]. Despite the many advantages of the emulsion polymerization process, some negative features are contrary to the goal of superior corrosion resistance. One of the point to take into account that surfactants. Surfactants effect to stabilization of emulsion, this can lead to water susceptibility. Also, polymerization does not happen exclusively in the latex particles. Polymerization can also occur in the water phase when water soluble monomers are present. This leads to hydrophilic oligomers and, therefore, increased water permeability of the resultant film. The resulting binder is a combination of polymer particles and a water phase that is highly influenced by the polymerization parameters [24,25]. Unfortunately, all the mentioned water soluble species can negatively influence the water sensitivity of the coatings and promote corrosion. Careful engineering of the polymer system, however, can minimize these potential

concerns. Proper choice of surfactants, monomers and polymerization conditions can provide polymer dispersions with superior corrosion resistance [25].

2.2 Ketonic Resins

Ketone and aldehyde resins are obtained by self-condensation of formaldehyde and aliphatic, cycloaliphatic, aliphatic-aromatic ketones or respectively aldehydes. In addition, further monomers, such as phenols and urea, also play a part. The aromatic hydrocarbon-formaldehyde resins are prepared from alkylated aromatic hydrocarbons, formaldehyde and other monomers [26]. The following monomers are given in Figure 2.2.

The resins are formed by polymerization of the vinyl ketones. Polymers having an alternating structure or by complex condensation reactions of the methylol compounds with one another or with further ketone molecules, leading to partially branched oligomers. Excess formaldehyde may lead to the reduction of the carbonyl group-to hydroxyl groups. Provided no substitution is carried out at the vinyl group, the polymerization activity of the vinyl ketone intermediate shows little dependence on the nature of the ketone employed. The industrial preparation of the resins is performed in reactors for condensation reactions, usually in a batchwise procedure [27,29].

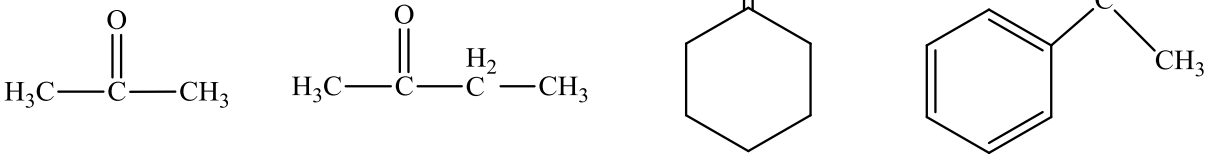
Ketone and aldehyde resins are used in large variety applications. In the coatings sector, the resins are used in combination with other binders, plasticizers, pigments and auxiliaries. The final formulations include marine saints, metal primers and wash primers, powder coatings and roadmarking paints. Further important applications are in recording and copying technology (toners), printed circuits, adhesives, binders for corrugated card, foundry moulding sands and laminates [28,29].

2.2.1 Aliphatic and cycloaliphatic ketone resins

Linear aliphatic ketones like methyl ethyl ketone and acetone are reacted to form resins with formaldehyde in particular. In the same way, methyl isobutyl ketone is used to produce resins for adhesives. Higher aliphatic ketones no longer form resins. As regards the cycloaliphatic ketones, cyclohexanone and methylcyclohexanone are the most important, although cyclopentanone, cycloheptanone and cyclic ketones with

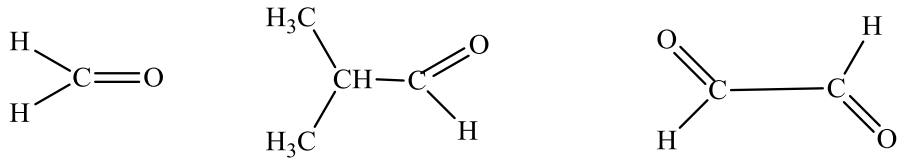
longer side chains have been described as raw materials for resins. Some of these type resins will be illustrated further parts [30].

A. Ketones



Actone | Methyl Ethyl Ketone | Cyclohaxanone | Acetophenone

B. Aldehydes



Formaldehyde | Isobutyraldehyde | Glioksal

Figure 2.2: Monomers using for keton aldehyde resins**.**

2.2.2 Methyl ethyl ketone formaldehyde resins

These resins are used in particular as binders for coatings and adhesives. They differ from resins based on cycloaliphatic or on aliphatic-aromatic ketones in their solubility and compatibility with other raw materials used in coatings. Their properties derive from the polarity of the ketone and from its specific behaviour during the alkaline-catalysed condansation.

The methyl ethyl ketone-formaldehyde resins possess a slight inherent coloration and are soluble in polar solvents such as alcohols, esters, ketones and glycol ethers. The resins are strongly polar and the softening range between 90 and 125 °C.

The resins are prepared by alkaline-catalysed condensation of methyl ethyl ketone and formaldehyde in a molar ratio of from 1:2 to 1:2.5 in a batch process, the ketone is reacted with formaldehyde in the presence of water. NaOH and KOH have proven to be the best catalysts for this reaction. The increase in the melting point from 80 to

120 °C can be achieved by raising the excess of formaldehyde. High softening points are also obtained by phase transfer catalysis. Special waning processes likewise lead to high-melting products that are light in colour.

The resins are often used together with film formers such as cellulose nitrate, acetylcellulose, cellulose ethers or natural resins. Among the properties endowed are, in particular, hardness, drying, sandability and good light stability. The resins possess the capacity to bring about gelatinization of cellulose nitrate. The free hydroxyl groups are exploring for crosslinking in isocyanate two-pack coatings, in adhesives and in moulding sands [30,31].

Methyl ethyl ketone formaldehyde resins can be mixted also with carbozels. Methyl ethyl ketone formaldehyde resins - carbazole comonomers on pyrite surface and the photoactivity behaviors and the inhibition effect of these coatings on the corrosion and photocorrosion of pyrite have been investigated. The protective action polymer film on the corroded surface can be envisaged in term of three effects: resistive, anodic and cathodic inhibition. Although PNVCz, prevents the corrosion cathodically, i.e. preventing the access of oxygen to the cathode reaction sites, Cz-MEKFR comonomer prevents the anodic reaction by preventing iron ions from the leaving the pyrite surface. PCz-MEKFR and PNVCz-MEKFR coatings on pyrite surface have a mixed type inhibition. Inhibition efficiencies of MEKFR modified carbazoles are independent in the way of synthesis and structure of resulting polymers when the results compared for P[Cz-MEKFR] and P[NVCz-MEKFR] [8-32].

2.2.3 Acetone formaldehyde resin

The greater resinification tendency of the unstable methylolation stages of acetone leads to a crosslinked, insoluble final structure. However, self-curing precondensates can also be prepared, which can be employed alone or in combination with other curable precondensates, such as phenol resols. Water-soluble products are obtained when acetone and formaldehyde are reacted in a ratio of 1 to 3. These products can be crosslinked under alkaline conditions [33].

Acetone-formaldehyde condensation products find a wide variety of uses in the adhesive bonding of paper and of wood. In these applications, phenol resols are often cocondensed in order to obtain chipboard and wooden materials with particular

weather resistance or to provide corrugated card with waterproof bonding. Further appli-cations of acetone precondensates are as photoreceptors in electrophotography and for the production of additives [34].

2.2.4 Cyclohexanone resins

Cyclohexanone and methylcyclohexanone have self-condensation properties. An aldol condensation takes place between the carbonyl group and the activated methylene group of a second molecule. The carbonyl group of the intermediates reacts with a further molecule of cyclohexanone; similar reactions follow until the final product is formed. The reaction can be catalysed by basic, acidic or neutral agents.

The softening points are between 80 and 120 °C. Under normal conditions the resins are resistant to acids and bases. But, under the action of acid they eliminate water at elevated temperatures and their properties are altered substantially. The cyclohexanone resins are lightfast, soluble in many solvents and compatible with the majority of raw materials. They are more expensive than cyclohexanone-formaldehyde resins.

In coating materials, the primary functions of cyclohexanone resins are to improve gloss and hardness. They may also increase weather resistance and the adhesion. The resins are added in quantities of from 5 to 50 per cent by mass to coating materials based on alkyd resins, vinyl chloride copolymers, chlorinated rubber, cellulose nitrate or oils. [29,31].

2.2.5 Cyclohexanone formaldehyde resins

Polyketone resin or named, as ketone-formaldehyde resin is one high-brightness, light-fastness of the neutral, non-saponification-based cyclohexanone - formaldehyde resin. Cyclohexanone can be reacted formaldehyde, to give methylol compounds or resinous products. In this case, the molar ratio and the reaction conditions which determine the properties of the products. A high formaldehyde excess promotes the formation of methylol compounds, whereas basic catalysis leads to resin formation [8].

Methylcyclohexanone or mixtures with aliphatic ketones and, more recently, trimethylcy-clohexanone have been applied. The modification of the resins with

phenols, epoxides, polyesters are known. Small beads are obtained by addition of dispersants. Hydrogenation and recovering with reducing agents are ways in which the light stability can be increased [34].

Cyclohexanone-formaldehyde resins do not have the broad compatibility and solubility of the pure cyclohexanone resins. Although they can no longer be combined with oils, combination with a range of important paint binders is possible. The use of methylcyclo-hexanone as a raw material usually leads to enhanced solubility and compatibility. By using trimethylcyclohexanone, resins can be obtained whose compatibility and solubility are virtually universal [29,34].

The cyclehexanone-formaldehyde resins can be combined with binder in the paint. The resins are used in order to improve drying, hardness, gloss and solids content properties when added on the binder. They can be used in wide range of application areas such as alkyd/acrylic coating materials, cement paints, epoxy resin systems and marine paints. In addition to conventional printing ink., UV-curing printing inks also play an increasing role. A further principal area of application is represented by adhesives and sealing compound. Another application which has been described is in optical recording media. The broad compatibility of resins based on trimethylcyclohexanone makes them ideally used to use in pigment pastes capable of universal application. The resins can be modified with many molecules for different purposes. Cyclohexanone-formaldehyde resins was in situ modified with using methyl isobutyl ketone, methyl ethyl ketone, methyl cyclohexanone, acetaldehyde, propion-aldehyde, cinnamaldehyde, dicynadiamide, arninotriazine and phenol [8,29].

Resins's performance can be increased with using small modifications. These modifications affect the adhesion on metal surface of paint. According to studies about resins show that, the number of –COOH group increases in ketonic resins, and long alkyl chain introduced the structure, well-adherent and more resistive coating can be obtained for metals. Although –COOH group that bound to aliphatic chain (AsCB6F) are effective for metal adhesion [32].

2.3 Corrosion Protection

Corrosion theorem can be though like a cell working, needed an anode and a cathode. The anode and cathode are different areas on the same piece of metal. A metal surface will have thousands of areas that are cathodes and corresponding areas

that are anodes. Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. As mentioned on Figure 2.3 the first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species is reduced, removing electrons from the metal. If any one of anode or cathode are isolated or removed, the reaction stops [35].

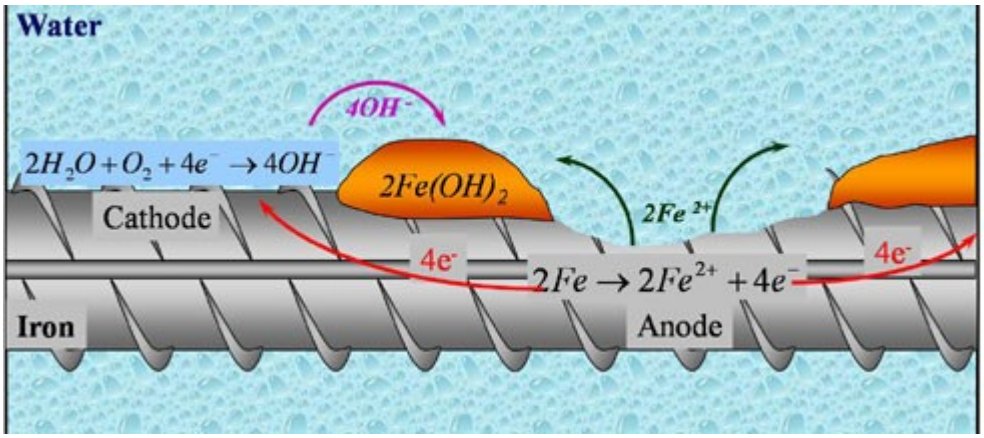


Figure 2.3: Corrosion formation on metal surface.

Corrosion is degradation of the properties of a material because of chemical reaction with the environment [36].

Metals have been used for centuries because of excellent properties. They have high strength and outstanding mechanical properties. For this kind of properties, metals can be used wide range of areas, such as: bridges, tanks, pipes, construction etc. However, when they are exposed to a corrosive environment, surface of the steel structures will corrode and thus pose a potential danger to the completely steel structure and reduce its service life [37].

For corrosion to happen the major component of steel, iron (Fe) at the surface of a component undergoes a number of simple changes. Firstly,

$$Fe \rightarrow Fe^{n+} + n \text{ electrons}$$

the iron atom can lose some electrons and become a positively charged ion. This allows it to bond to other groups of atoms that are negatively charged. Wet steel rusts to give a variant of iron oxide, also iron's electron can easily react with atoms or molecules in the environment, like water and oxygen. So the other half of the reaction of iron must involve water (H_2O) and oxygen (O_2) something like this;

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Negatively charged material that can combine with the iron and electrons, which are produced in the first reaction are used up. Iron hydroxide occurs with this reaction.

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$$

Oxygen dissolves quite readily in water and because there is usually an excess of it, reacts with the iron hydroxide and hydrated iron oxide as know as brown rust comes off.

$$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3.H_2O$$

Sometimes corrosion occurs over the majority of the surface of a metal at a steady and often predictable rate. Metal becoming thinner and usually alters the appearance of the surface. It causes failure mechanical strength of the components or reduces wall thickness until leaking results [37,38]. Although it is unsightly, its predictability facilitates easy control, the most basic method being to make the material thick enough to function for the lifetime of the component. This type of corrosion can be slowed or stopped by using below things;

1. Slow down or stop the movement of electrons

a) Coat the surface with a non-conducting medium such as paint, lacquer or oil

b) Reduce the conductivity of the solution in contact with the metal an extreme case being to keep it dry. Wash away conductive pollutants regularly.

c) Apply a current to the material.

2. Slow down or stop oxygen from reaching the surface. Difficult to do completely but coatings can help.
3. Prevent the metal from giving up electrons by using a more corrosion resistant metal higher in the electrochemical series. Use a sacrificial coating which gives up its electrons more easily than the metal being protected. Apply cathodic protection. Use inhibitors.
4. Select a metal that forms an oxide that is protective and stops the reaction [39,40].

Sometimes corrosion can be more severe because the failure occurs without warning and after a surprisingly short period of use or exposure. DIN EN ISO 8044 defines 37 different forms of corrosion. Some more known ones are explained below [41].

2.3.1 Corrosion types

2.3.1.1 Atmospheric corrosion

It is the most visible of all corrosion processes. Accounts of them are more failures in terms of cost and tonnage than any other type of material degradation processes. Atmospheric corrosion can occur all time and every places such as industrial, marine, rural, indoor areas. Corrosion occurs uniformly over a wide area of the metal surface producing a general thinning of the metal leading to eventual failure.

2.3.1.2 Galvanic corrosion

This can occur when two different metals are placed in contact with each other and is caused by the greater willingness of one to give up electrons than the other. Three special features of this mechanism need to operate for corrosion to occur:

• The metals need to be in contact electrically

• One metal needs to be significantly better at giving up electrons than the other

• An additional path for ion and electron movement is necessary.

Prevention of this problem is based on ensuring that one or more of the three features do not exist.

a) Break the electrical contact using plastic insulators or coatings between the metals.

b) Select metals close together in the galvanic series.

c) Prevent ion movement by coating the junction with an impermeable material, or ensure environment is dry and liquids cannot be trapped.

2.3.1.3 Pitting corrosion

Pitting corrosion occurs in materials that have a protective film such as a corrosion product or when a coating breaks down. The exposed metal gives up electrons easily and the reaction initiates tiny pits with localised chemistry supporting rapid attack. It is a localized attack, where the rate of corrosion is greater at some areas than at others. This is caused by differences in potential between different points on the metal surface. A brake in an oxide film protecting a metal surface can cause pitting attack. Control can be ensured by:

a) Selecting a resistant material

b) Ensuring a high enough flow velocity of fluids in contact with the material or frequent washing
c) Control of the chemistry of fluids and use of inhibitors
d) Use of a protective coating
e) Maintaining the material's own protective film [41,42,43].

2.3.2 Corrosion prevention techniques

Metal surfaces are protected with some precaution methods. These are listed below.

2.3.2.1 Water treatment

-de-aeration: Oxygen can be removed from water by desecration. It is frequently applied to boiler-feed water used for boilers operating at high temperature. At temperatures existing in these boilers, even small amounts of oxygen present a serious corrosion problem. Deaeration is also used on some water flood supply waters in which the presence of oxygen presents a critical problem.

-degasification: It is a general term applied to the removal of dissolved gases such as carbon dioxide and H_2S. these dissolved gases are either removed entirely or their concentrations reduced to such a value that they do not contribute significantly to corrosion. In instances where sour water is the only available supply for injection water, it is necessary to remove H_2S. Otherwise, corrosion may form iron sulphite that will eventually plug the formation rock in the injection well.

-water softening: In addition to removing calcium and magnesium ions, the lime and soda ash process for water softening removes dissolved carbondioxide. The pH of most water softened by this method is increased. This may also contribute to reducing corrosion [44,45].

2.3.2.2 Addition of inhibitors

Corrosion inhibitors are chemical substances that are added to the corrosive environment to reduce or eliminate corrosion. Corrosion inhibitors are typically divided into three categories: anodic inhibitors, cathodic inhibitors, and organic inhibitors. Anodic inhibitors, made up of chromates, nitrites, molybdates, alkali phosphates, silicates, and carbonates, act by minimizing the anodic part of the corrosion reaction. These inhibitors form an insoluble protective film on anodic surfaces to passivate the steel. Cathodic inhibitors, consisting of zinc, salts of

antimony, magnesium, manganese, and nickel, form an insoluble film on the cathodic surfaces of the steel. They are usually less effective than anodic inhibitors, but are also safer. Organic inhibitors, amines, esters, and sulfonates, block both the anodic and cathodic reaction on the entire surface of the metal [44].

2.3.2.3 Cathodic protection

Cathodic protection consists of applying an electrical current to the surface of the metal to be protected in such a way that it will become a cathodic area. The current is applied externally, so that a net positive current enters all areas of the metal, including those that were previously anodic. Cathodic protection is applied to protect steel, brass, lead, copper and aluminium against corrosion when these metals are immersed in water. Cathodic protection is particularly useful in protecting the submersed areas of water tanks and filters. Since only the areas below the water line are protected, other methods must be used to protect metal above the water line. Cathodic protection has an advantage over coatings in protecting sand filters, since coatings will not stand sand abrasion during backwashing operations[39].

2.3.2.4 Coatings

The most common and cost effective steel protection method used throughout the world is coatings. Steel is so widely used that some form of coating protection must be used in order to increase the life expectancy of steel structures, piping or conduit. Removing or separating the corrosing environment from the metal can prevent corrosion. This is the principle of coatings applied for corrosion protection. Paint and galvanizing are examples of coatings that have been used for many years.

Coatings can be divided into 3 general categories:

-Metallic coatings:

Most metal coatings are applied by dipping the article into a molten bath of the metal or by electroplating the coating from aqueous solution. Some coatings are also applied by metal spraying. Metal coatings can be classified as noble or sacrificial. A noble metal coating such as chrome plating protects by its own resistance to corrosion. Sacrificial coatings such as zinc and cadmium cathodically protect the base metal.

-Inorganic coatings:

Vitreous enamels, cement lining, phosphate coatings and oxide coatings represent inorganic coatings. Vitreous elements or glass coatings are very corrosion-resisted but somewhat brittle. Cement coatings are very popular for lining water flow lines.

-Organic coatings:

Organic coatings are the most widely used means of protecting against corrosion. These coatings represent a large variety of materials that can be classified as paint, enamel, lacquer, and plastic linings. In recent years, plastic linings have found frequent usage in protecting tubing, flowlines, and tanks from corrosion. The surface preparation and application of these coatings is very important in the success of the coating [46-47].

2.3.3 Water based corrosion protection

Solvent borne resins are leader in the anticorrosive industry but water-based anticorrosion resins have gone through many stages of evolution. People need converge to water-based binders for corrosion production because of volatile organic content (VOC) limits. The more stringent environmental standards are pushing waterborne anticorrosive protection. In addition, waterborne coatings are the reduction of worker exposure to organic solvents and of fire hazards in confined areas. Despite steady progress, water borne technology is still need for improvements for reaching the equal performance with solvent borne resins. Recent innovations in the area of polymer colloids and hybrid materials offer new opportunities to develop novel coatings for metal protection [1,48].

There are some important things, before protection a substrate from corrosion. These points provide fast and accurate solution for protection of metals. The points are explained in to the ISO 12944 International standard for Paints and varnishes -- Corrosion protection of steel structures by protective paint systems. Understanding ISO environment conditions can help to tailor specifications, ensuring coatings are not under or over specified and saving unnecessary cost. ISO 12499 determines 3 critical sections to corrosion protection; environment conditions, type of substrate and durability [49].

Paint producers who are responsible of the metal protection coating system, firstly determine atmospheric or environment conditions. According to ISO 12499 corrosive environment is divided 5 selections as Table 2.2 [49].

Table 2.2 : Corrosive environment according to ISO 12944.

C1 / C2	Heated buildings/neutral atmosphere, Rural areas, low pollution
C3	Urban and industrial atmospheres, Moderate sulphur dioxide levels, Production areas with high humidity
C4	Industrial and coastal, Chemical processing plants
C5I	Industrial areas with high humidity and aggressive atmospheres
C5M	Marine, offshore*, estuaries, coastal, areas with high salinity

Application areas are divided as regard to pollution, humidity and salinity. Corrosion environment types are showing C marks like C1, C2 etc. Pure acrylic water borne system is recommended for C1,C2 and C3 areas. These areas are less humidity and pollution and ideal for do it yourself applications or light to medium industrial applications. For more aggresive conditions such as marine coatings and aggressive environment industrial areas that are marked as C4 and C5, solvent borne or 2 pack systems are provide more protective way.

As shown on the Figure 2.4 below, water based coating protection can be used mid and light-duty areas and these correspond to C1; C2 and C3. Protective high humidity and aggressive salinity areas like marine industry preffers solvent-based systems instead of water borne based.

According to ISO 12944 Water based corrosion protection, corrosion protection durability time can be divided 3 parts.

High durability: >15 years to first major maintenance

Medium durability: 5-15 years to first major maintenance

Low durability: <5 years to first major maintenance

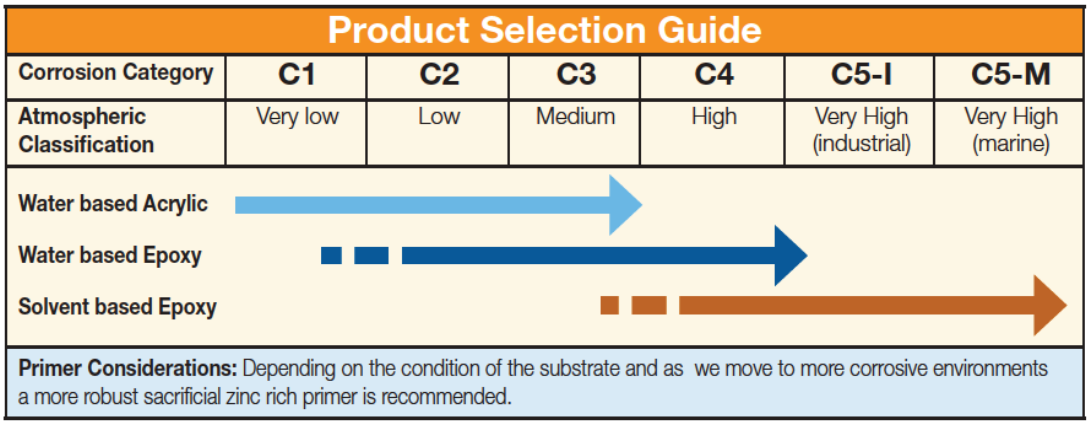


Figure 2.4 : Product performances according to corrosion conditions.

The corrosion protection of metal is often obtained by multi-layer systems involving at least a primer and a top coat. These two coats are often based on different technologies implying solvent borne and water borne binders and formulations. It introduces complexity in the applications and drying equipment and processes. Epoxies, urethanes, alkyds and acrylics can be used as a resin in metal coatings [50].

The principal properties required to metal coating is that; for a primer are adhesion, corrosion and water resistance. Concerning the top coat, the main properties are exterior UV durability, lack of dirt pickup, chemical resistance and gloss. Developing a binder, that can be used as single Direct to Metal coating (DTM) will fit with this last parameter of sustainability. By choosing the appropriate technology, it is possible to design acrylic binders for waterborne metal coatings with improved barrier properties, low water uptake, and improved anticorrosion properties [51].

Waterborne acrylic dispersions are mainly used in mid and light-duty coatings for the maintenance (bridges, plant and industrial equipment, repainting, towers etc.), transportation (trucks, buses, trains, tractors, mining trucks etc.) and DIY (repair, general maintenance, steel building panels etc.) segments among others. These coatings are applied as multicoat systems or one coat systems. Multicoat systems are composed of three layers [52]:

•Primers, having the function of providing good corrosion protection and adhesion to the metal surface

•Intermediate coats, act as a barrier to moisture and aggressive chemicals and help to build film thickness

•Topcoats, responsible for the aesthetics, but also for better impermeability and weatherability

Alternatively a monocoat may be applied, the so called direct to metal (DTM) coatings, with minimal surface preparation. DTM coatings are attractive due to the reduction of application steps (no surface preparation and only one applied coating), the reduction of raw material costs (one coat versus many) and the lack of the necessity of using active pigments. DTM coatings, however, do not often display the superior properties of a multi coat system and are typically used in lighter duty applications [53].

2.3.4 Water based metal coating

Direct-To-Metal (DTM) coatings functions as both primer and topcoat in just one coating. Aim is that, obtained some quality and performance with using one coat application. DTM paints are applied on metal without using any primer. Thus, they have to provide good adhesion to the metal substrate, corrosion resistance, and aesthetic properties including gloss and durability. In addition, one coat application provides cost reduction for industrial areas. DTM acrylic coatings are VOC compliant and durable long-term protection. They also feature the same fast-drying properties as other waterborne coatings do [54].

2.3.5 Test methods

2.3.5.1 Salt spray

According to ASTM B117 test method, metallic corrosion can be measured with using salt spray machine. This machine applied salt solution on the metal surface under humidity and high temperature. Metal panels put on the machine and their corrosion performance is measured by time. After a certain time metal panels are evaluated according to blistering, adhesion and corrosion performance. The apparatus for salt spray exposure consists of a fog chamber, a salt solution reservoir, a supply of suitably conditioned compressed air, one or more atomizing nozzles, specimen supports, provision for heating the chamber, and necessary means of control. Drops of the solution that accumulate on the ceiling or cover of the chamber shall not be permitted to fall on the specimens being exposed. Drops of solution that

fall from the specimens shall not be returned to the solution reservoir for re-spraying [55].

2.3.5.2 Immersion test

Immersion test is quite simple version of salt spray test. Accordance with ASTM B895, 5% NaCI solution is prepared and test panels are immersed on the salty water. Metal panels are tested under ambient temperature (22°C ± 3°C) and relative humidity conditions (50% ± 10%) in salty water. After a time, panels are took out from salty water solution and evaluated according to blistering, adhesion and corrosion performances [56].

2.3.5.3 Electrochemical method

Electrochemical corrosion testing measures and/or controls the potential and current of oxidation/reduction reactions. More specifically, when a metal is immersed in a given solution, electrochemical reactions characteristic of the metal-solution interface occur at the surface of the metal, causing the metal to corrode. An electrochemical potential, called the corrosion potential or the open circuit potential that can be measured in volts occurs with these reactions. Since the corrosion potential is determined by the specific chemistry of the system, it is a characteristic of the specific metal-solution system [57].

2.3.5.4 Weathering test

Long term exposure to sunlight leads to the degradation of materials. Exposure of the UV light is generally results in breaking down the polymer chains. This frequently results in a deterioration of the physical properties, changes in color or chalking of the part surface. If the polymer chain breaking down that affects all performance of coating material. For this reason polymers or coating material can be referred, have to be resistance of the weathering conditions. Weathering test machines simulate real extreme atmospheric conditions; UV, humidity and rain. Metal coating if applied on the external place have to be resistance of weathering tests. Metal panels' corrosion performance can be also measured with weathering test machines. These machines applied UV light, high humidity and simulate rain conditions at the same time. ISO 4892/3 standard gives details about weathering tests [58].

3. EXPERIMENTAL PART

Pure acrylic polymer is used as a binder. This polymer is synthesized by emulsion polymerization method. Ketonic resin is synthesized and a blend is prepared with polymer and ketonic resin. Pure acrylic polymer and acrylic polymer-ketonic resins blend is tested in high gloss metal coating formulation. Coating formulation as can be called metal paint is applied different kind of metal surface for testing adhesion and corrosion resistance.

3.1 Materials

An anionic, water soluble surfactant that the chemical composition is polyoxyethylene tridecyl phosphate ester. This surfactant can be dissolved in the water and it provided from Organik Kimya.

Acrylic acid is a clear, colorless liquid with a characteristic acrid odor. It is miscible with water, alcohols and ethers. Acrylic acid as shown on Figure 3.1 will undergo the typical reactions of a carboxylic acid, as well as reactions of the double bond similar to those of the acrylate esters. It lends itself to polymer preparation as well as use as a chemical intermediate.

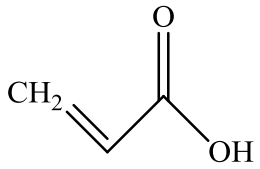


Figure 3.1 : Acrylic acid.

Methacrylic acid structure is showing on Figure 3.2. Also MAA is a clear colourless liquid and can be soluble in water. Those of acrylic acid and metacrylic acid provide electrosteric stabilization during the polymerization process. Acrylic acid and methacrylic acid is ordered from Arkema. Methyl Methacrylate is a monomer, Tg value is 105°C. It is very hard monomer, has good chemical resistance and weathering stability. Chemical composition is as Figure 3.3 as shown below.

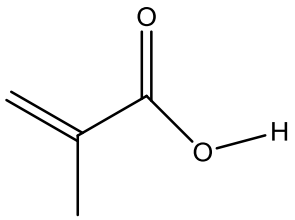


Figure 3.2 : Methacrylic acid.

Acrylic acid and methacrylic acid is ordered from Arkema.

Methyl Methacrylate is a monomer, Tg value is 105°C. It is very hard monomer, has good chemical resistance and weathering stability. Chemical composition is as Figure 3.3 as shown below.

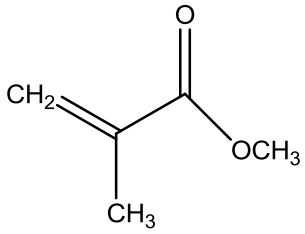


Figure 3.3 : Methyl Methacrylate.

2-Ethylhexyl acrylate is another monomer which is used to emulsion polymer synthesized. It is readily polymerized and displays a range of properties dependent upon the selection of the monomer and reaction conditions. It gives good water resistance, low temperature flexibility and excellent weathering and sunlight resistance to emulsion polymers. Tg value is -85°C. Chemical composition is figure at Figure 3.4.

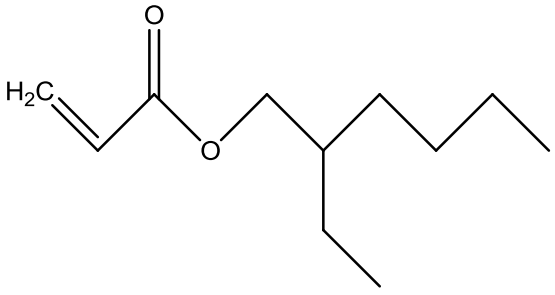


Figure 3.4 : 2-Ethylhexyl acrylate.

Monomers are provided from Organik Kimya without giving any brand name.

Amonyum persulfat is an initiator. Its role is that making free radicals to provide polymerization proceed. Amonyum persulfate is provided from Organik Kimya without giving any brand name.

Sodium Formaldehyde Sulfoxylate which received from Brueggemann Chemicals is a formaldehyde-free reducing agent. It is capable of substantially reducing free monomers, reaction time and yellowing. Tert-Butyl hydroperoxide is a oxidatative and used with Sodium Formaldehyde Sulfoxylate for redox reaction, buying from Sigma Aldrich.

Chlorisothiazolinone / Methylisothiazolinone is a biocide that protect of the emulsion polymers against to fungi and bacteria. It is provided from THOR.

In Figure 3.5, Cyclohexanone is a organic compound, it come by Sigma Aldrich.

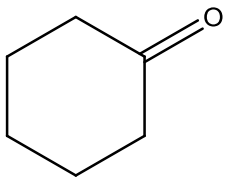


Figure 3.5 : Cyclohexanone.

Cyclohexane is a cycloalkane. It is delivery from Sigma Aldrich.

Formaldehyde shown in the Figure 3.6

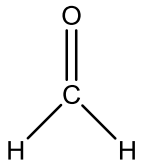


Figure 3.6 : Formaldehyde.

Dispersion Agent's is to disperse all pigments and fillers into the paint formulation. Sodium salt of a carboxylate polyelectrolyte based dispersing agent is used in the formulation and it is buying from Tego.

For wetting agent, a non-ionic acetylenic diol surface active agent are chosen in this part, Tego's wetting agent is used.

Propylene glycol is the most popular open time agent in paint formulations, purchased from Sigma Aldrich.

Silicon oil defoamer is used in the grinding stage, mineral oil one is used with the polymer mixing, both of them is chosen from Tego.

Rutile type titanium dioxide is used in the paints, Kronos 2310 is preferred in this study is supplied from Kronos.

Talc and kaolin are filler. Both of them are supplied from Omya.

Thickeners are adjust paint flow behavior. In this study polyurethane based one is selected, PUR 40 is used as a defoamer and it is purchased from Münzing Chemie.

Dowanol DPnB is used in the formulation as a co-solvent, it is taken from Dow.

Flash rust inhibitor protects the paint from early rusting. Sodium nitrite based 33% solution is used in the metal paint, it is supplied from Raybo.

3.2 Polymer Synthesis

Core-shell polymer morphology is selected in this thesis. Polymer synthesis occurs in two steps, emulsion 1 and 2. Firstly emulsion 1 is prepared. For this aim, 7 gram anionic surfactant (30% solution) is measured on a beaker and 120 gram water is put in and mixed with a scraper. 2 gram acrylic acid, 6 gram methacrylic acid are added on the surfactant-water mixture. 120 gram MMA, 180 gram 2-EHA is added on the beaker. 50 gram of the mixture are weighed in a another beaker and waited. 1 liter flask is cleaned and dried and after 250 gram water is weighed. Flask is put on the heater, automatic blender is started and waiting until 82°C. APS is diluted with water 2:49 amounts and it is used as a catalyzator. This catalyzator is feed on the flask through another neck of flask. 10 gram anionic surfactant and 50 gram of the 1th emulsion are added on the heat water during water mixing. Acid and monomer mixture are feed on the flask within 1 hours. Reaction conditions must be stable for avoiding gelling. Temperature must be 82°C and blender works continuously. Meanwhile second emulsion preparation is done. For second emulsion, 100 gram 2-EHA, 200 gram MMA is weighed. 120 gram water, 7 gram anionic surfactant,8 gram MAA is weighed on the beaker and monomers are added on to it. After finishing first emulsion, second emulsion mixture is feed on the same reaction conditions. Feed is done after 1 hour and take the emulsion to rest but blender is still working and temperature is 82°C. After 30 minutes later redox step is started. t-BHP and Sodium Formaldehyde Sulfoxylate is diluted with water and feeding on the flask. Only 10 minutes these are mixed and then heater and blender are shut down. For the last step, biocide is added on the emulsion. CIT/MIT type of biocide is selected for this

reaction and added 1,4 gram. pH is checked and adjusted almost 8 with ammonia. Figure 3.7 shows the structure of acrylic emulsion polymer.

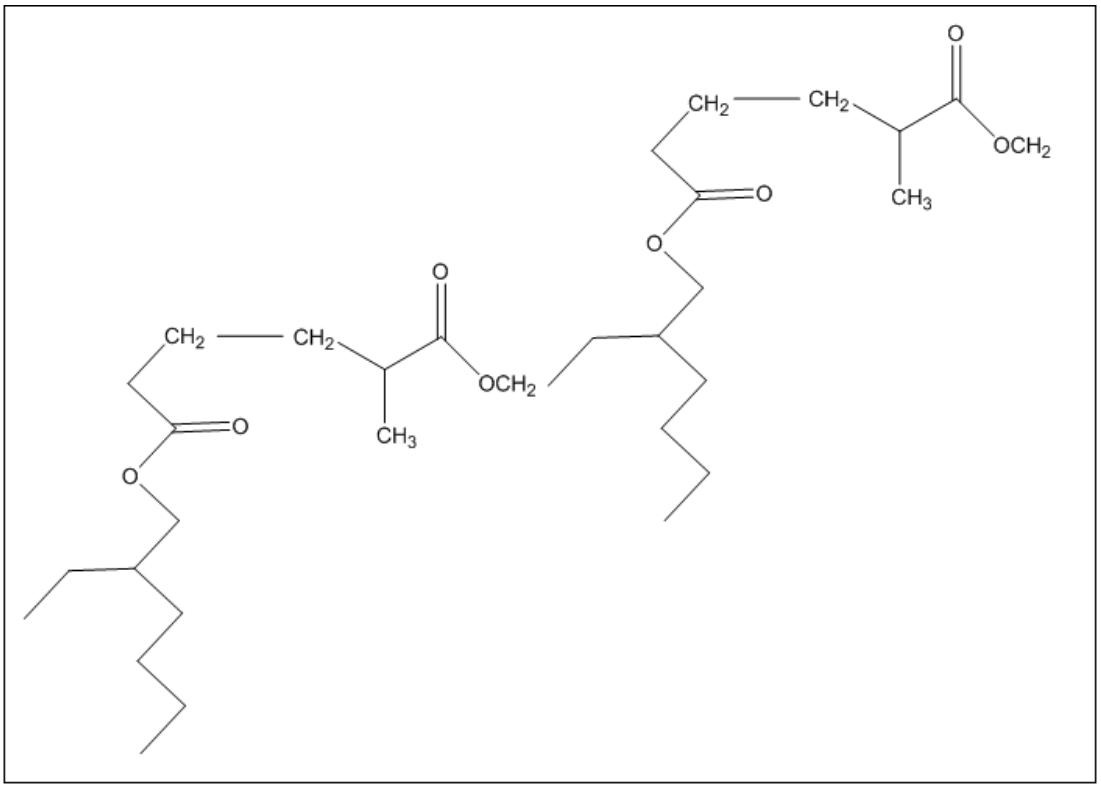


Figure 3.7 : Polymer structure.

3.3 Synthesis of Cyclohexanon Formaldehyde Resin

Cyclohexanone-formaldehyde resin is selected as a ketonic resin because of high amount hydroxyl content. Ketonic resin is synthesized under atmospheric conditions with using three neck flask, mechanical mixer and water-bath heater. 1 mole (104 ml) Cyclohexanone, 25 ml cyclohexan, 30 ml 37% formaldehyde solution is placed to three neck flask. 5 ml, 20% NaOH solution is prepared. 0,75 ml prepared NaOH solution is added on the flask drop by drop until pH 9-10. Dropping funnel is placed on a neck. Temperature is adjusted 70 $^{©}$C with heater. System is mixed by continuously. When the reflux occurs, 3.5 ml NaOH is added on 100 ml formalin (A solution of formaldehyde in water) and this formalin is added dropwise on the system within 15 minutes. Reaction temperature is increased 80-85°C. 3 hours later reaction is done. Firstly, mixture appearance is homogeneous, then it becomes milky and later it becomes putty like. During the reaction pH must be 9-11 ranges, temperature must be 80-85°C and mechanical mixer must be worked continuously. The water

resulting from the reaction is drawn away by decantation. Rest of resin is washed off with hot water. Then it is dried at 110°C for 2 hours. After 2 hours, it is dried again at 75 at vacuum oven for 2 hours. Cooled resin is stored under ambient temperate. This resin is hard and powder form. It is diluted with acetone before adding the polymer.

Two different methods are used for blending ketonic resin on the polymer. First one is after synthesized resin, ketonic resin is diluted with acetone with 1:1 rate. This solution is added on acrylic polymer as 5:95 rates (5 resin, 95 polymer). 700 gram polymer is weighted and added 36,8 gram resin solution under high speed mixer during 10 minutes.

Second method is ketonic resin reaction is terminated after 2 hours later. Resin does not dired under 110°C to dehydration and taken out as emulsion form. This emulsion gets hard in time at room temperature and it must be heat at 70°C before adding on polymer. After heat the ketonic resin, puted nonionic surfactant on it as 0,1% amount under high speed mixture. Then ketonic resin is added on polymer emulsion 5% amount.

3.4 Metal Coating Formulation

Water based paint is used in this study. For testing of polymer-ketonic resin blend performance, Table 3.1 paint formulation is prepared. This formulation is a gloss paint formulation that has high amount binder amount. Any anticorrosive pigments have not in this formulation due to evaluate only binder and ketonic resin performance on metal protection.

In this thesis 3 different paints are prepared. Firstly, only acrylic polymer is used into the paint. Secondly, acrylic polymer ketonic resin blend is added on paint formulation and acrylic polymer commercial resin is added on paint. In this way, 3 paints are evaluated between each other.

First of all, water is measured on the 1 liter cup, the cup put under the high speed mixer which is called a dispermat and it is opened. Dispersing agent, ammonia, wetting agent, open time agent and defoamer are measured carefully and added on the water in a sequence. This mixure is stirred under 700 rpm speed within 10 minutes.

Table 3.1 : High gloss paint formulation.

Ingredients	**Amount (g)**
Water	50
Dispersion Agent	7
Ammonia	2
Wetting Agent	1
Open-Time Agent	7
Defoamer	2
Titanium Dioxide	107
Talc	27
Kaolin	45
Thickener	5
Polymer – Ketonic Resin	690
Co-solvent	45
Ammonia	2
Flash rust inhibitor	6
Defoamer	3
Thickener	1
TOTAL	1000

After 10 minutes titanium dioxide, talc and kaolin are added on the system and increased the speed as 1300-1500 rpm. After 15 minutes, speed is decreased as 750 rpm and then added polymer. After adding polymer-ketonic resin mixture, all other ingredients such as co-solvent, ammonia, flush-rust inhibitor, defoamer and thickener are added and this mixture is stirred 10 minutes within 750 rpm. 10 minutes later high speed mixture is closed and paint is ready for testing.

3.5 Initial Testing

Water based paint is prepared in this study. For testing of polymer-ketonic resin blend performance, water-based paint formulation is prepared according to Table 3.1.

After prepared the water-based paints, they are applied on the four different metal substrates: stainless steel, aluminum, galvanized steel and cold rolled steel. Paints are applied on metals 100 micron on wet film. After applied paint on metals, metals are cured 7 days at ambient conditions. Ambition condition is meaning that 23±2°C and 50±5 % relative humidity. After 7 days, metal panels are cruss cut with the device which is shown Figure 3.8. Adhesion performance is checked on aluminum, galvanized, stainless steel metals and cold rolled steel with a tape. Following the ISO 2409 method, a quotation of zero means perfect adhesion and a quotation of five means complete loss of adhesion. These results will be shown under the results title.

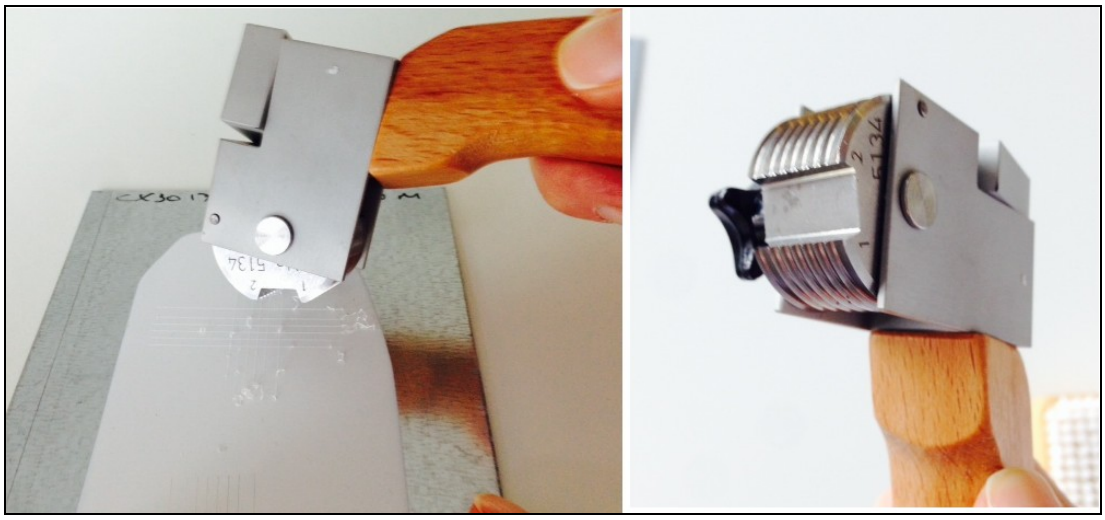


Figure 3.8 : Cross-cutter device.

Dry and wet adhesion are checked on different kind of metal types. Wet adhesion test is done with wet napkins. Figure 3.9 shows applied paint on different metal types and wet adhesion test.

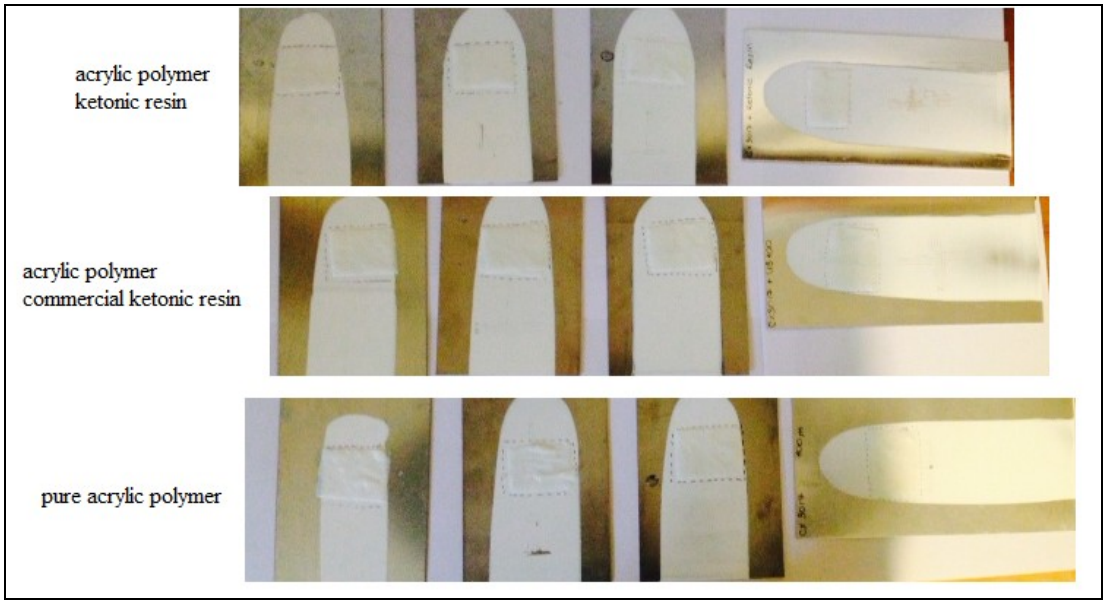


Figure 3.9 : Paints on different metal types and wet adhesion test.

Corrosion test can be done with salt spray machine. In this test, cold rolled steels are put on the salt spray machine and after 92 and 250 hours later, taken from the machine and evaluated according to ISO 9227. In this study, for getting only pretesting results, cold rolled steel has coated and cured 7 days at room temperate. After curing time 5% NaCI solution is prepared and all cold rolled metals are immersed on salty water as half-length.

4. RESULTS AND DISCUSSION

Permeability of coatings to water and oxygen are affected by monomer's hydrophobicity. A higher glass transition temperature (Tg) is preferable for reducing oxygen and water permeability. For this reason most hydrophobic monomers are selected for polymerization. Methyl methacrylate (MMA) and butyl acrylate (BA) are used in the laboratory trial. Core-shell morphology is designed with these monomers. Core is softer than shell because giving elasticity to coating material. For these reason, 2-EHA ratio is higher. Shell is designed with higher methyl metacrylate ratio. Shell must be harder than core because it must be durable against other conditions, like corrosion, UV light, water.

Two different acids are used. These are AA and MMA. Acid are decrease blistering effect and improve adhesion.

Anionic surfactants are selected. NH_3^+ is used in synthesis. Because, for iron, the anode reaction is shown in equation, where iron is oxidized to the ferrous ion.

$Fe = Fe^{++} + 2e^-$

Reduction occurs at the cathode. An example is the reduction of hydrogen ion, shown in $H^+ = ½\ H_2 – e^-$ equation. For this reason anionic surfactant is selected.

For reduction of hydrogen ion, NH_4OH are used instead of NaOH. NH_4OH is used as neutralization agent.

Ketonic resin selection is done according to hydrogen amount. For this reason formaldehyde ketonic resin is selected. Ketonic resin is a solvent base system and it is difficult to mix it with water based acrylic polymer. For getting good blend, a surfactant is selected and added on ketonic resin system. Marlipal, alkylpolyethylene glycol ethers nonionic surfactant, is added on ketonic resin system then ketonic resin-polymer blend is prepared. Another way, blend cannot be stable.

Water based paint is used in this study. General paint formulations are composed of four main components. These are binder, pigment, filler, solvent (water). Also additives must be added in the formulation. These additives are dispersing agents,

defoamers, reology modifiers etc. Anticorrosive paints have also flash-rust inhibitor additives for protecting of metal surface from early rusting. Moreover, some post-additives such as co-binders can be added in the formulation for improving performance. In this thesis, ketonic resin is used as co-binder additive.

Low PVC paint formulation is designed for testing polymer-ketonic resin performance. PVC means that pigment volume concentration and formulation is shown below equation (2.1):

$$PVC\ \% = \frac{100\ x\ V_{pigment}}{V_{pigment} + V_{non-volatile\ binder}} \quad \textbf{(4.1)}$$

If we increase the binder amount, PVC will decrease. Using low PVC paint formulation provides to evaluate effect of the binder on the corrosion protection much better.

Water is used as a mobile phase for water based paints, solvents are used in the solvent based paint as a mobile phase. Water based and solvent based differentiation is specified according to mobile phase. Tests are done with water based formulation. Dispersion Agent's main function is to disperse all pigments and fillers into the paint. Also, they avoid pigment agglomeration and provide paint stabilization. Sodium salt of a carboxylate polyelectrolyte based dispersing agent is used in the formulation.

Wetting agent helps to dispersion agent to wetting pigment and fillers. A non-ionic acetylenic diol surface active agent are chosen in this part.

Open-Time agent slows down the evaporation of water. Paint applicators need a time for repainting brush or roller marks which occur during application. Propylene glycol is the most popular open time agent in paint formulations.

Defoamer prevents to formation of excessive surface foam or microfoam during preparation, handling and transport. Defoamers can be divided two parts; mineral oil and silicone oil based. Mineral oil defoamer has less activity than silicon oil defoamers. Silicon oil defoamers can be added during titanium dioxide grinding because it is very active and can be caused some surface defects. Mineral oil defoamers are more compatible, less activity so they can be added during polymer

mixing stage. Silicon oil defoamer is used in the grinding stage, mineral oil one is used with the polymer mixing.

Titanium Dioxide is a pigment. It occurs in two crystal forms: anatase and rutile. Anatase is less expensive than rutile type because of refractive index. Refractive index of anatase is 2.55 and rutile is 2.7. So rutile gives better hiding power and it has lower UV activity. Rutile type titanium dioxide is used in the paints [59].

Talc and kaolin are filler. They have different refractive index, density and crystal form but both of them have plateles surface. Plateles surface slows down water penetration than cubic or rhombohetral surfaces. For increase adhesion performance on paint, these type of fillers are preferred more. Both of them increase paint volumes and obtained good film body with getting together. Talc is a magnesium silicate and used to paint for preventing shiny effect. Kaolin is an aluminum silicate and used for helping hiding power and weather resistance.

Thickeners are adjust paint flow behavior. In this study polyurethane based one is selected. Polyurethane thickener is used in gloss paint and wood coating formulations.

Co-solvent referred to as film-forming aids or coalescent, decreases minimum film formation temperature of the polymer. These co-solvents are added on the polymer for getting proper film after curing. After evaporation these co-solvents do not remain in the film, these are emitted by environment at different rates depending on ambient temperature, atmospheric humidity and boiling point, and on the resulting vapour pressure. Dowanol DPnB (Dipropylene glycol n-butyl ether) is used in the formulation as a co-solvent. This paint is need a cosolvent because the polymer's Tg temperature is measured 55°C and for getting proper film formation at room temperature.

Ammonia used as a neutralizing agent. Paint system generally alkaline, pH values are between 8 and 9. pH values important for pigment stabilization.

Flash rust inhibitor protects the paint from early rusting. Flash rusting is corrosion from steel bleeding through a coating creating a stain within hours of the coating application. Long term corrosion is not flash rusting. Flash rusting occurs when a thin film of water resides on the surface of steel for a brief period causing corrosion to take place. The corrosion products are often soluble and can migrate within a

coating to produce a stain. It should be noted that steel can be found in many coatings applications other than the main substrate. Sodium nitrite based 33% solution is used in the metal paint.

4.1 Polymer Analysis Results

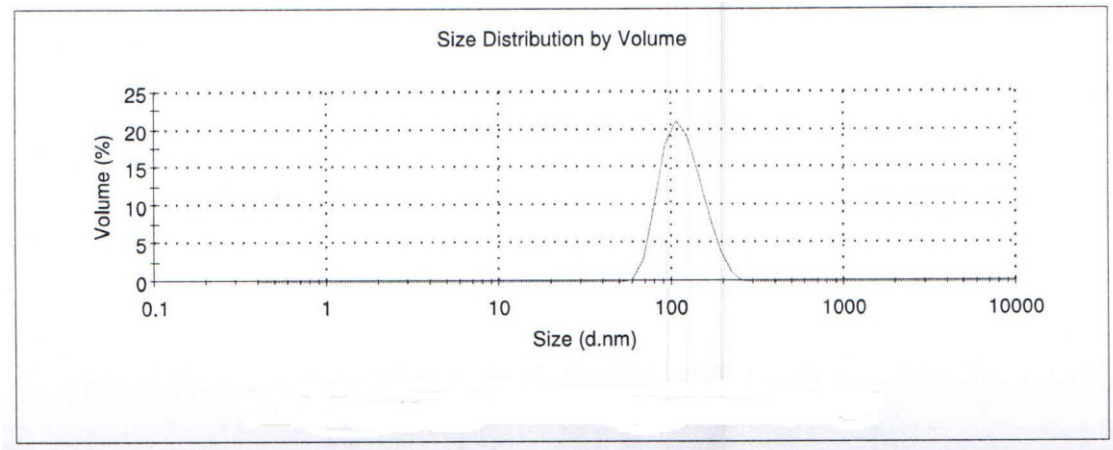
Acrylic polymer which is synthesis with emulsion polymerization method, analyzed on the laboratory. Table 4.1 is summarized polymer analysis results on below. Size distribution graph of polymer, Tg value of polymer, FTIR and H-NMR results of polymer are mentioned next parts. As shown on the table, high solid amount polymer is synthesized. Polymer pH value is 7-8 and this value is fit for paint preaperation. FTIR results shows that polymer combosition is formed of MMA and 2-EHA monomers. Tg values is 55°C and MFFT is 22°C, these data shows that polymer is hard enough for metal coating. There is not see any problem to size distrubition graph, polymer is ok for particle size.

Table 4.1 : Polymer analysis results.

Solid	48%
pH	7-8
FTIR	MMA – 2 EHA
Tg	55°C
MFFT	22°C
Particle size	118 nm

4.1.1 Size distribution graphic of acrylic polymer

According to size distribution results, acrylic polymer's particle size is measured 118 nm and witdh of the particle is 32.59 nm. Graphic is shown in Figure 4.1. As hown on the graph, particle size distrubition is uniform.



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	121,7	Peak 1:	118,0	100,0	32,59
PdI:	0,031	Peak 2:	0,000	0,0	0,000
	0,949	Peak 3:	0,000	0,0	0,000

Figure 4.1: Size distribution by volume graphic of polymer emulsion.

4.1.2 DSC thermal analysis of acrylic polymer

DSC results are operated with one cycle. The cycle was heated -5^{o}C to 85^{o}C with 10^{o}/min heating rate. In this study, as it is seen in the Figure 4.2, T_g value of polymer is determined as 55 ^{o}C. Graphic is shown on the Figure 4.2.

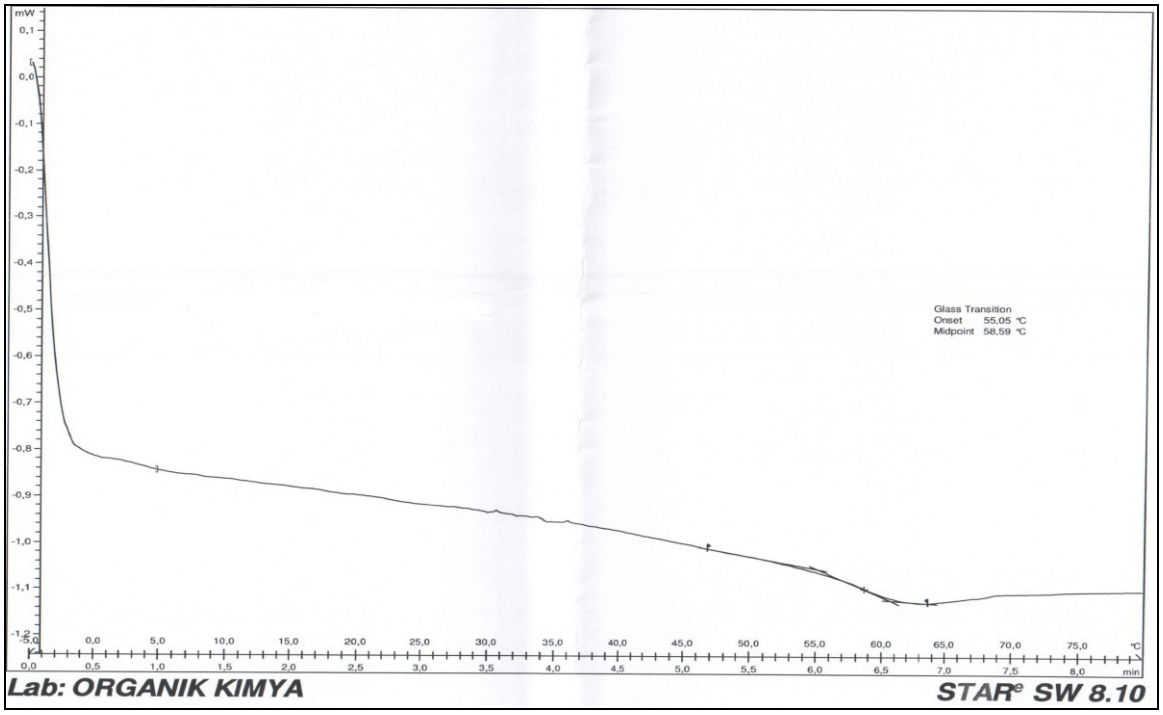


Figure 4.5 : Tg values of polymer emulsion.

4.1.3 FTIR analysis of acrylic polymer

As shown on the Figure 4.3. in this study, charectristic peaks were observed at 2954 cm^{-1}, 1727 cm^{-1}, 1448 cm^{-1} and 1142 cm^{-1}. Observed the presence of the compound obtained with CH_2-CH_3 groups are observed 2954 cm^{-1}, the presence of COO group in 1727 cm^{-1}, C≡O is observed at 1227 cm^{-1}, 1500 cm^{-1} and below is accepted finger print area and C-0 groups are in this range.

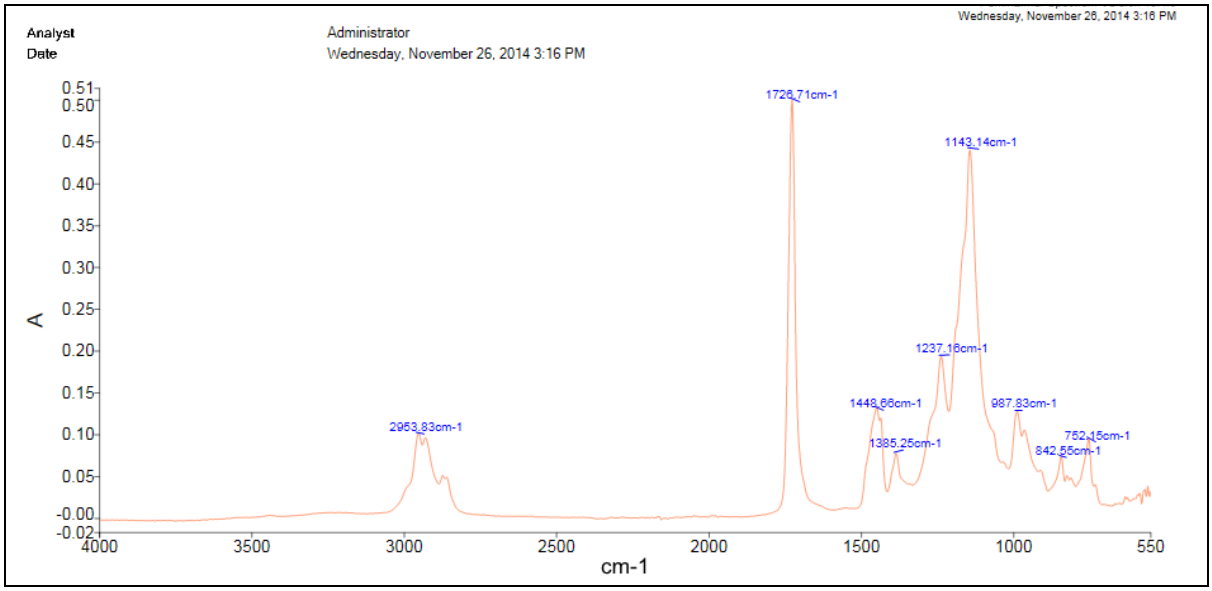


Figure 4.6 : FTIR specktrum of polymer emulsion.

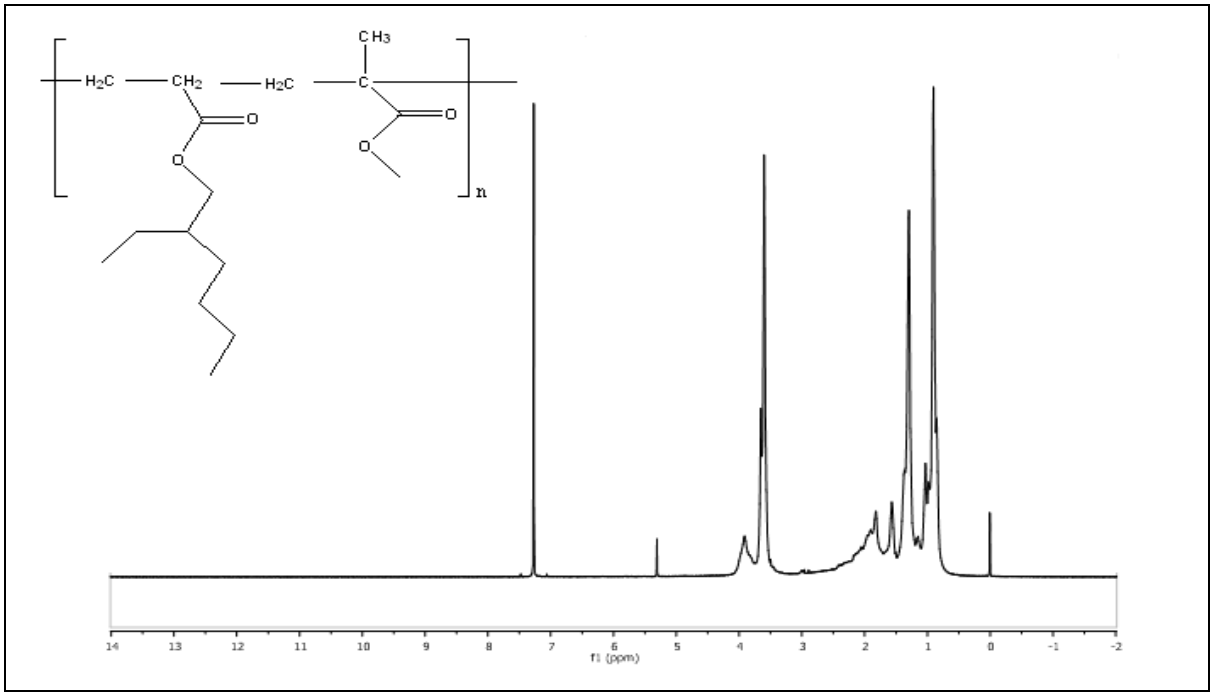


Figure 4.4 : ^{1}H-NMR spectrum of acrylic polymer.

4.1.4 ^{1}H-NMR analysis of acrylic polymer

The ^{1}H-NMR spectra were recorded from the deutareted solvent solution which is chloroform, $CHCl_3$. As shown on the Figure 4.4. aliphatic carbon groups such as CH_2 and CH_3 are observed 1-2 ppm. OCH_2 groups which are coming from MMA end group and 2-EHA's middle, are observed at 3.8 ppm.

4.2 Ketonic Resin Analysis Results

4.2.1 ^{1}H-NMR spectroscopy of CFR

The ^{1}H-NMR spectra were recorded from the deutareted solvent solution which is $CDCl_2$ and it shown the Figure 4.5. The peaks are appearing at about 1.1 – 2.4 ppm were due to the aliphatic -CH_2 and –CH groups, 3.2 – 4.2 ppm due to the –CH_2 methylen bridges and methyl groups, 4.5 – 4.8 ppm due to the –OH groups of the methyl groups.

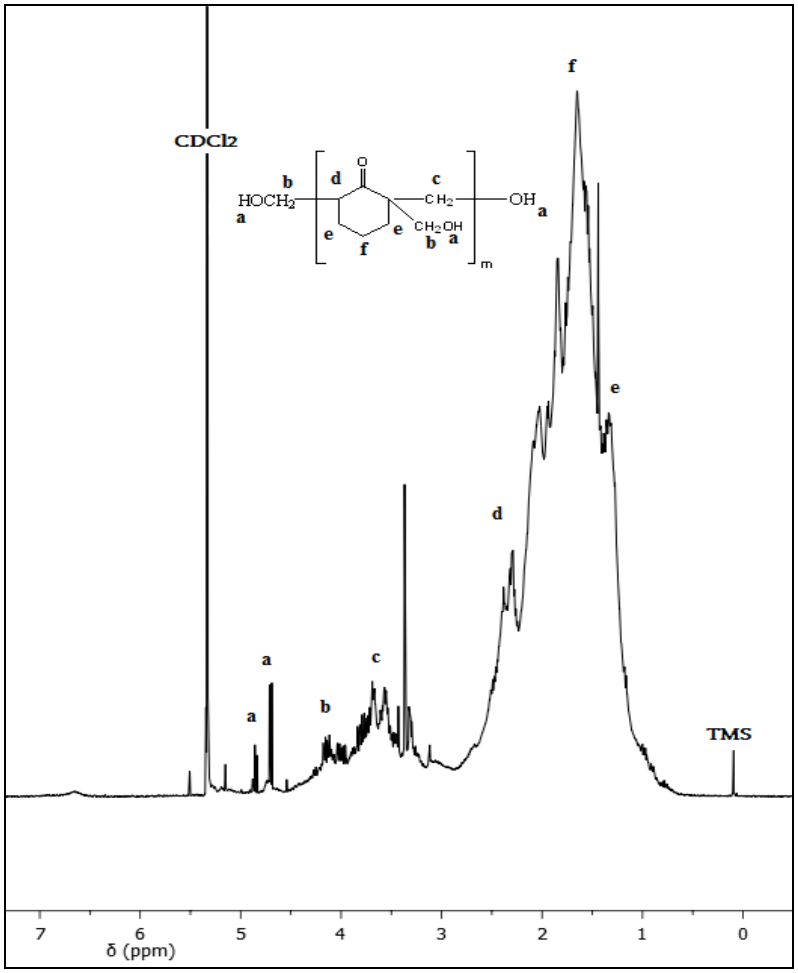


Figure 4.5: ^{1}H-NMR spectrum of CFR

4.2.2 FTIR-ATR spectroscopy of CFR

In this study, charectristic peaks were observed at 3399 cm^{-1}, 2925 cm^{-1}, 1699 cm^{-1} and 1445 cm^{-1}. These peaks respectively attributed to hydroxy methyl groups, aliphatic $–CH_2$, carbonyl C=O, and $–CH_2$ methylene bridges. Also between 970-1200 cm^{-1} three main peaks were observed which belongs to the C-O stretch between methylne bridges and cyclohexanone ring. The spectrum of the synthesized pure resin was given in the Figure 4.6. These charecteristic wavelenghts of the pure CF resin and observed wavelenghts of the pure CF resin were given in the Table 4.2.

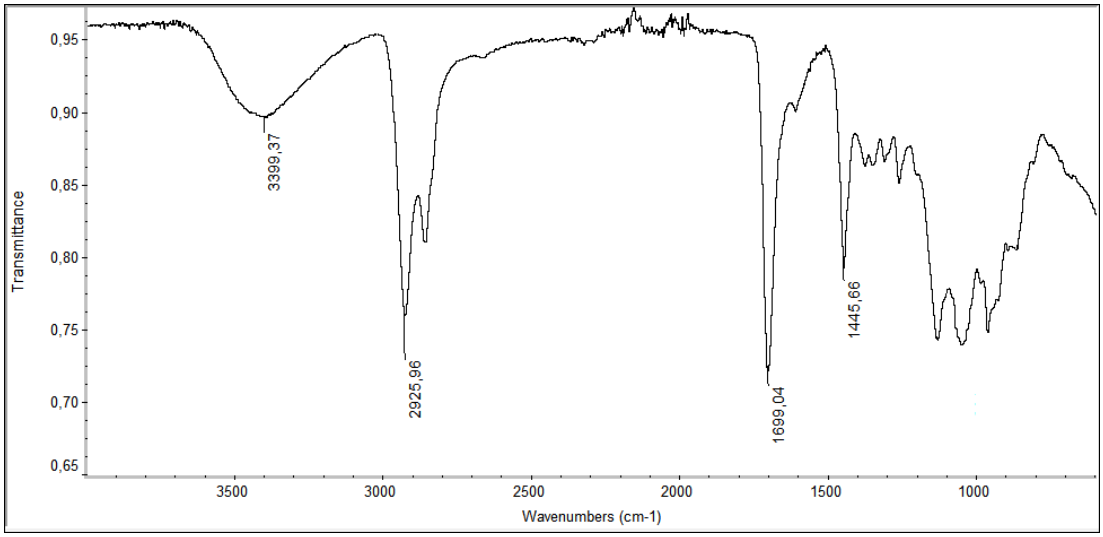


Figure 4.6: FTIR spectrum of CFR

Table 4.2: Characteristic literature wavenumber values and observed wavenumber values of of CFR.

CFR		
Literature wavenumber values, cm^{-1}	**Observed wavenumber values, cm^{-1}**	**Functional group**
3400	3399	-OH
2920	2925	Aliphatic –CH2
1700	1699	Carbonyl C=O
1450	1445	$–CH_2$ methylene bridge

4.2.3 DSC thermal analysis of CFR

DSC results of CFR was operated with one cycle. The cycle was heated 30°C to 300° with 10°/min heating rate. In the literature T_g value of CFR is about 30°C [2011]. In this study, as it is seen in the Figure 4.7, T_g value of CFR was determined as 45 °C. Charectristic peaks were observed at 3399 cm^{-1}, 2925 cm^{-1}, 1699 cm^{-1} and 1445 cm^{-1}.

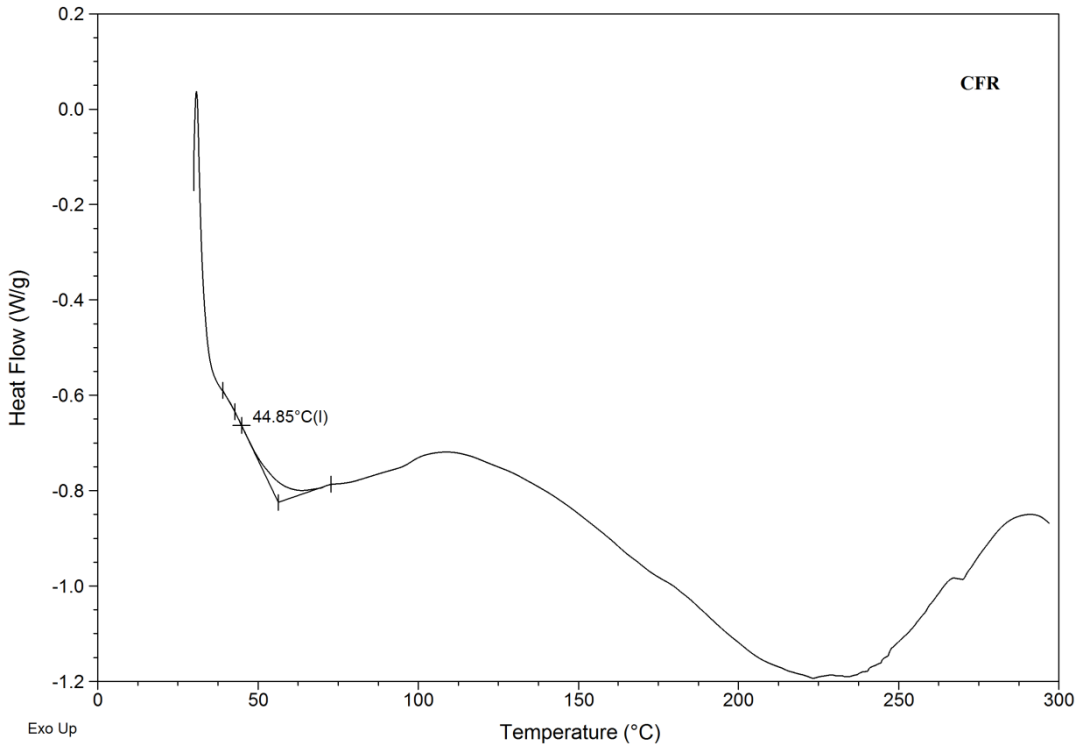


Figure 4.7: DSC thrmogram of CFR.

4.3 Paint Analysis Results

Paints solid and pH values are shown on Table 4.3.

Table 4.3 : Paints analysis results.

Solid	51%
pH	8.2

Adhesion performance are evaluated according to ISO 2409 and corrosion performance are tested according to immersed water test. All results summarized on Table 4.4 and adhesion photos are showed Figure 4.7-8-9-10.

Table 4.4 : Paints test results

	Pure acrylic polymer formulation		Acrylic polymer – ketonic resin formulation		Acrylic polymer – commercial ketonic resin formulation	
Adhesion test	**wet**	**dry**	**wet**	**dry**	**wet**	**dry**
Aluminum	5	1	1	3	3	2
Galvanized	1	0	0	0	0	0
Stainless steel	5	1	5	1	5	1
Cold rolled steel	5	0	3	0	5	0

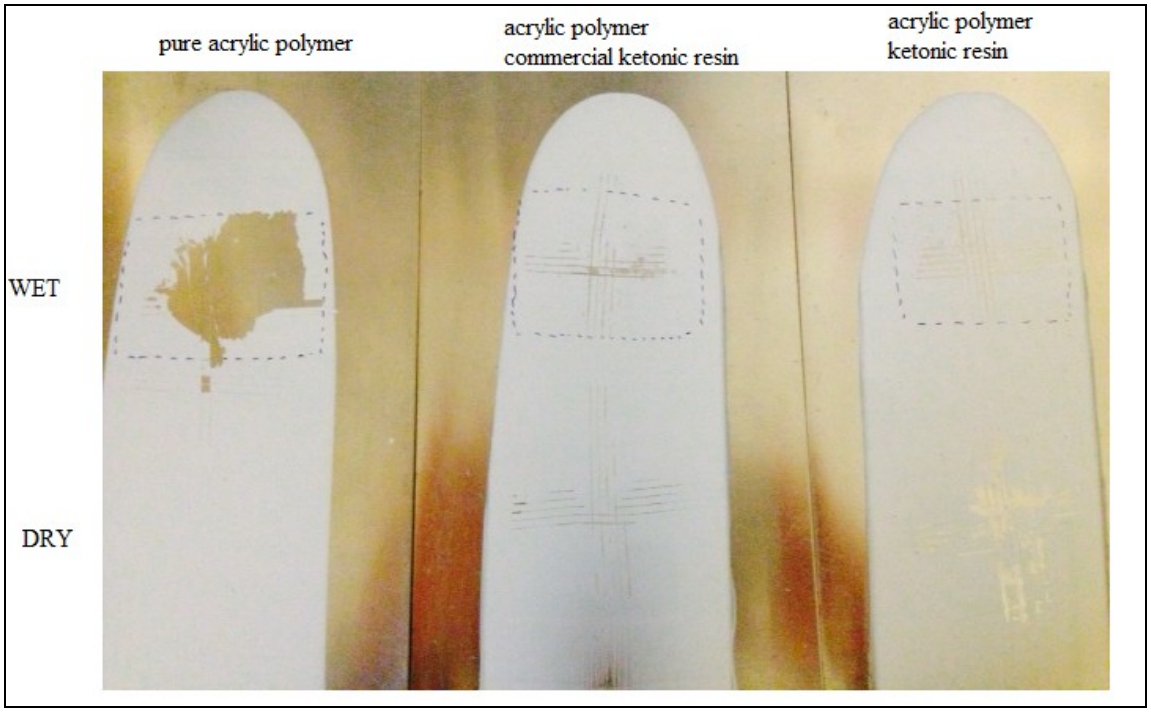


Figure 4.8 : Adhesion on aluminum.

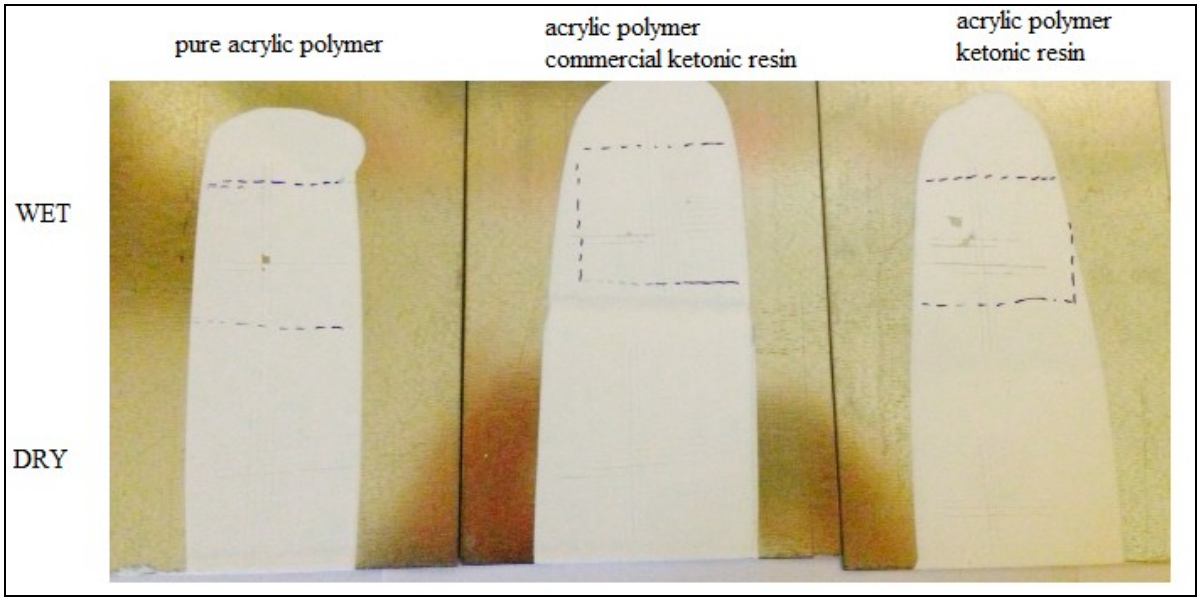


Figure 4.9 : Adhesion on galvanized steel.

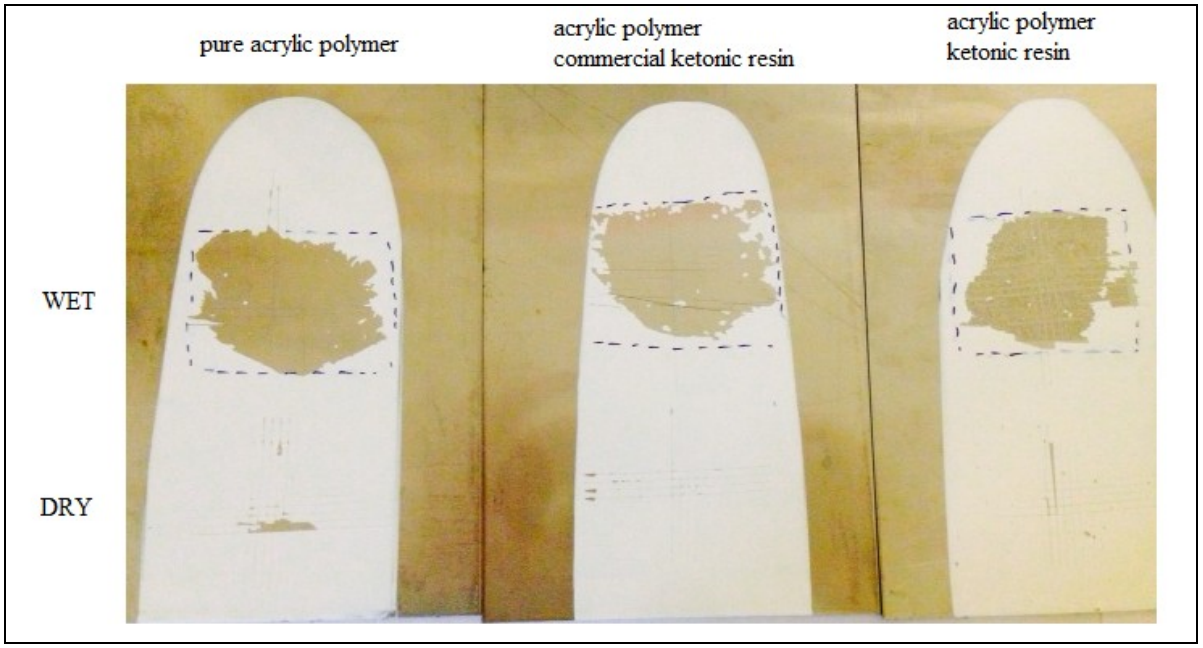


Figure 4.10 : Adhesion on stainless steel.

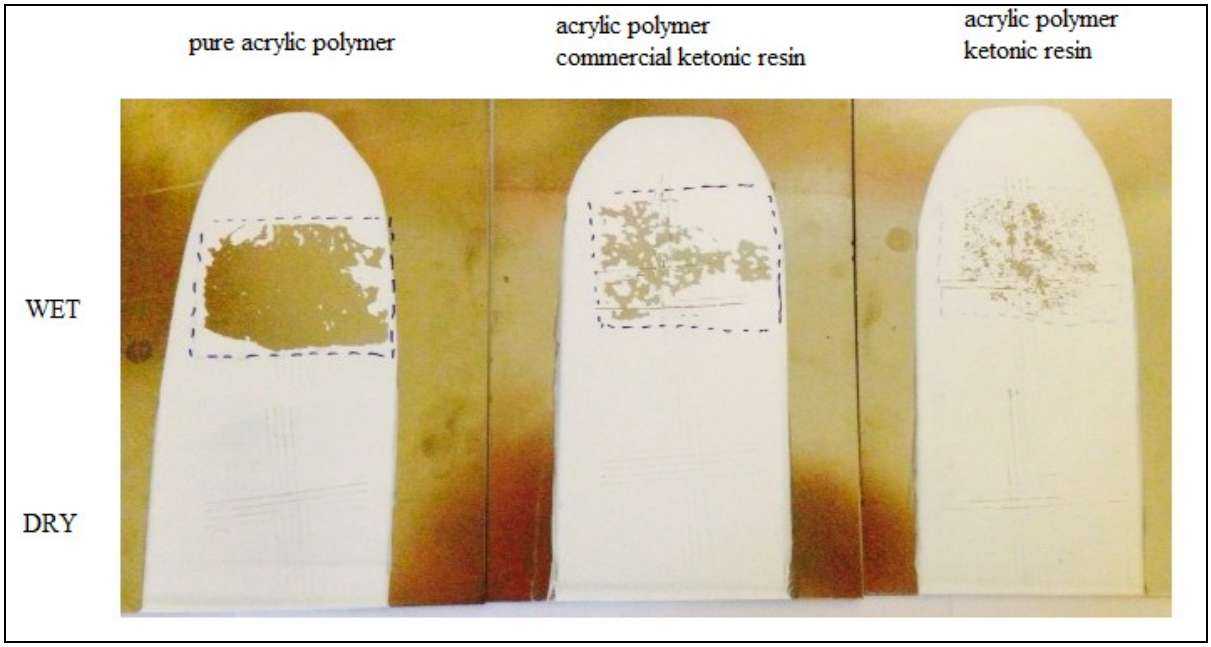


Figure 4.11: Adhesion on cold colled steel.

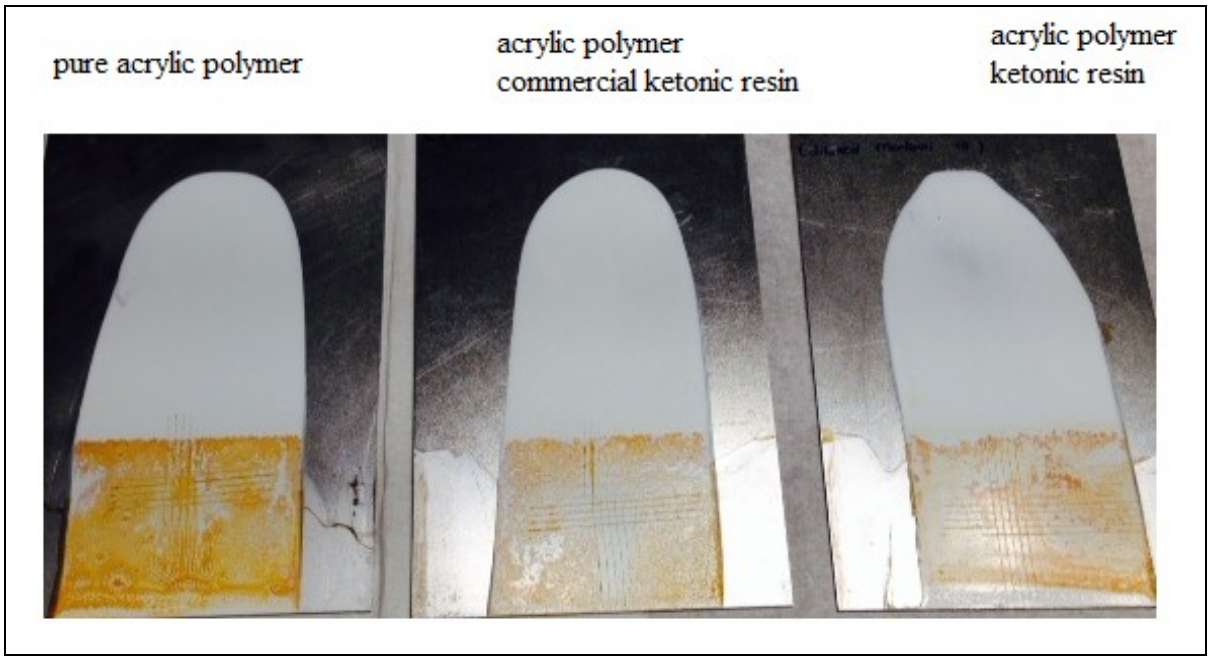


Figure 4.12 : Corrosion test resuls.

5. CONCLUSION

Metals are chosen a wide range of industrial area due to excellent mechanical properties for getting durable physical structures. Corrosion is the one of the most crucial effect that decreases their service life. Metals have to be protected from corrosion with some protection methods. Generally metals are coated with metal protected paint for decreases corrosion. Solvent borne system is chosen for metal protection but some environmental regulations impose limitation their usage. Water borne system comes into play in this stage. They still need for improvements to achieving same performance with solvent borne system. Choosing right polymer is one of the important criteria for corrosion protection and polymers have to be supported with additives.

The aim of the thesis is synthesis a pure acrylic polymer with emulsion polymerization method. Also, synthesis a ketonic resin as a paint additive for increasing adhesion. Last step is the evaluation of polymer and ketonic resin into a paint formulation and checking adhesion and corrosion performances.

Core-shell morphology is selected and MMA and 2-EHA are used as monomers into emulsion polymer. MMA gives high strength mechanical properties and 2-EHA gives flexibility to polymer. Ketonic resins are added to the emulsion polymer to prolong coating life because gives good adhesion and corrosion properties. Cyclohexanone formaldehyde resins have the most hydroxyl group than the other ketonic resin ones. This speciality provides an interaction with water-borne system. Cyclehexanone formaldehyde resin is blended with acrylic polymer 5% amount.

Cyclehexanone formaldehyde resin performance is checked into paint formulation for showing contribution on adhesion and corrosion performance. Paints are applied on four different metal types for checking adhesion performance. Corrosion performance is checked on only cold rolled steel metals.

According to cross cut test, ketonic resin is increased the wet adhesion on aluminum and colled rolled steel. Stainless steel adhesion cannot improve with adding ketonic resins. Adhesion on galvanized is excellent for all paints. Colled rolled adhesion performance is best with ketonic resin, also if comparing ketonic resins, synthesis one and commercial one, with each other, synthesis ketonic resin shows best adhesion performance. If compared pure acrylic polymer with polymer-ketonic resin system as corrosion resistance, synthesis ketonic resin with acrylic polymer blend gives better adhesion and blistering performance than the others. This shows that ketonic resin is increase adhesion on metal especially on hard conditions like salty water.

There is some incorporation on paint when adding ketonic resin on polymer with blending method. Next step will be adding ketonic resin during the acrylic polymer synthesis to connecting each other with chemical bonds.

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